

Levels and trends of flame retardants in the Swedish environment

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Doctoral thesis
Swedish University of Agricultural Sciences
Uppsala 2017

Acta Universitatis agriculturae Sueciae

2017:90

Cover: The pathway of flame retardants from rivers into the thesis (E. Ribeli)

ISSN 1652-6880

ISBN (print version) 978-91-7760-070-1

ISBN (electronic version) 978-91-7760-071-8

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Print: SLU Service/Repro, Uppsala 2017

Levels and trends of flame retardants in the Swedish environment

Abstract

Flame retardants (FRs) are compounds used in, e.g., electronics and furniture to prevent fires. Due to leakage, FRs are widely spread in the environment and several FRs have been found to be environmentally persistent, bioaccumulative and toxic. As a result, legacy FRs such as polybrominated diphenyl ethers (PBDEs) have been banned, and replaced by alternative FRs with often similar properties as the banned ones. The aims of this thesis were to develop an analytical method for the analysis of alternative FRs, to assess the current FR pollution in Sweden, and to improve the understanding of transport and fate of FRs within boreal catchments. In Paper I, gas chromatography (GC) coupled to tandem mass spectrometry (MS/MS) using an electron impact (EI) ion source was concluded to provide the best overall sensitivity, for most analysed FRs, including halogenated FRs (HFRs), organophosphorus FRs (OPFRs) and PBDEs. Alumina was found to be the superior material for clean-up of FR-containing extracts. In Paper II, Oasis HLB eluted with dichloromethane (DCM) was concluded to provide the highest overall recovery for the extraction of FRs from water. A high influence (both positive and negative) of natural organic matter (NOM) on extraction recovery was observed for all extracted FRs when extracted from NOM-containing water. The influence appeared to be systematic and the formation of a NOM-sorbent layer and the ability of certain FRs to form strong hydrogen bonds are suggested to be key mechanisms when extracting FRs from NOM-containing water. The concentrations of FRs in Swedish rivers were investigated in Paper III. Σ FR concentrations ranged up to 170 ng L^{-1} (mean $31 \pm 45 \text{ ng L}^{-1}$) with generally higher concentrations in the south (latitude $<62^\circ\text{N}$) than in the north (latitude $>62^\circ\text{N}$). Several OPFRs are suggested to undergo long-range atmospheric transport (LRAT). Daily fluxes of FRs into the Baltic Sea were estimated to be 8.8 kg day^{-1} and comprised mainly tetrabromobisphenol-A (TBBPA), 3,4,5,6-tetrabromophthalic anhydride (TEBP-Anh), and 2,4,6-tribromophenol (TBP). This is presumably the first time environmental detection of TEBP-Anh is reported and it is suggested to originate from nearby airports. In Paper IV, elevated FR concentrations were observed in streams and rivers during spring flood and hydrophobicity fractionation was observed during snowmelt. HFR concentrations were generally higher at a mire site than at a forested site.

Keywords: flame retardant, gas chromatography, mass spectrometry, solid-phase extraction, natural organic matter, long-range atmospheric transport, seasonal change, hydrophobicity fractionation, boreal catchment

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Koncentrationer och trender av flamskyddsmedel i den svenska miljön

Abstract

Flamskyddsmedel (FR) är kemiska ämnen som används i t ex elektronik och möbler för att förhindra bränder. På grund av läckage är många FR allmänt spridda i miljön och flera FR har konstaterats vara svårnedbrytbara i miljön, bioackumulerande och giftiga. Detta har lett till att t ex polybromerade difenyletrar (PBDEer) förbjudits, och ersatts av alternativa FR med ofta liknande egenskaper som de förbjudna FR. Målen med denna avhandling var att utveckla en analysmetod för att analysera i huvudsak alternativa FR, att utvärdera hur förorenad den svenska miljön är av FRs, samt att förbättra kunskapen om hur FR transporteras i boreala avrinningsområden. Slutsatsen från Paper I var att gaskromatografi (GC) kopplat till tandem masspektrometri (MS/MS) med elektronisk jonisering (EI) gav bäst känslighet vid analys av de flesta halogenerade FR (HFR), organofosfat-FR (OPFR) och PBDEer. Alumina konstaterades vara det bästa materialet för rening (clean-up) av extrakt som innehåller FR. I Paper II gav Oasis HLB (med diklormetan för eluering) de högsta utbytena vid extraktion av FR från vatten. Naturligt organiskt material (NOM) hade stor påverkan (både positiv och negativ) på utbytena av samtliga FR vid extraktion från vatten som innehöll NOM. Påverkan verkar vara systematisk och bildandet av ett NOM-sorbent lager samt förmågan hos vissa FR att bilda vätebindningar föreslås vara viktiga mekanismer vid extraktion av FR från vatten som innehåller NOM. Vid en undersökning av FR i svenska älvar (Paper III) sågs sammanlagda FR koncentrationer upp till 170 ng L^{-1} (medelvärde $31 \pm 45 \text{ ng L}^{-1}$) med generellt högre koncentrationer i söder (latitud $<62^\circ\text{N}$) än i norr (latitud $>62^\circ\text{N}$). Det fanns indikationer på att flera OPFR kan undergå långväga atmosfärisk transport. Den dagliga transporten av FR till Östersjön uppskattades till 8.8 kg dag^{-1} , främst bestående av tetrabrombisfenol-A, 3,4,5,6-tetrabromftalat anhydrid (TEBP-Anh) och 2,4,6-tribromfenol (TBP). Detta är troligen första gången som TEBP-Anh detekterats i miljön och det föreslås komma från närliggande flygplatser. I Paper IV uppmättes förhöjda FR-koncentrationer i vattendrag under vårfloeden och en hydrofobicitetsfraktionering skedde under snösmältningen. HFR-koncentrationerna var generellt högre i vattendraget som avvattnade en stor andel myrmark jämfört med det med enbart skog.

Nyckelord: flamskyddsmedel, gaskromatografi, masspektrometri, fast-fas extraktion, naturligt organiskt kol, långväga atmosfärisk transport, årlig variation, hydrofobicitetsfraktionering, borealt avrinningsområde

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Dedication

Till Farmor, Mamma, Pappa, Sandra, Marcus och Simson

Science is fun. Science is curiosity. We all have natural curiosity. Science is a process of investigating. It's posing questions and coming up with a method. It's delving in.

Sally Ride, American astronaut

Contents

List of publications	9
Abbreviations	11
1 Introduction	13
1.1 A brief history of flame retardants	13
1.2 Why should we care about flame retardants?	14
1.3 The chemistry of flame retardants	16
1.4 Legacy flame retardants	17
1.4.1 PBDEs	17
1.4.2 PBBs	18
1.5 Alternative flame retardants	24
1.5.1 HBCDD	24
1.5.2 TBBPA	24
1.5.3 Other alternative flame retardants	25
2 Overall aim of the thesis and objectives of Papers I-IV	39
3 Methods	41
3.1 Extraction and elution	44
3.2 Sample clean-up	46
3.3 Instrumental analysis	47
3.4 Quality assurance and quality control	48
4 Results and discussion	51
4.1 Analysis of flame retardants	51
4.1.1 Extraction of flame retardants from water (Paper II)	51
4.1.2 Clean-up (Paper I)	53
4.1.3 Instrumental analysis (Paper I)	54
4.2 Sources and trends of flame retardants (Paper III)	58
4.2.1 Levels of flame retardants in Swedish rivers	58
4.2.2 Fluxes of flame retardants to the Baltic Sea	61
4.2.3 Point sources of flame retardants	61
4.2.4 Environmental variables	62

4.3	Flame retardants in a pristine boreal catchment (Paper IV)	63
4.3.1	Levels in stream and river water	63
4.3.2	Impact of hydrological events	66
4.3.3	Influence of land-cover type	66
4.3.4	Potential drivers of flame retardant concentrations in boreal streams and rivers	68
5	Conclusions and future research	69
	References	75
	Popular science summary	81
	Populärvetenskaplig sammanfattning	85
	Acknowledgements	89

List of publications

This thesis is based on the work contained in the following papers, referred to by Roman numerals in the text:

- I Jakob Gustavsson*, Lutz Ahrens, Minh A. Nguyen, Sarah Josefsson, Karin Wiberg (2017). Development and comparison of gas chromatography-mass spectrometry techniques for analysis of flame retardants. *Journal of Chromatography A*, 1481, pp. 116-126.
- II Jakob Gustavsson*, Lutz Ahrens, Minh A. Nguyen, Sarah Josefsson, Dan Berggren Kleja, Karin Wiberg (2017). Influence of natural organic matter on the extraction efficiency of flame retardants from surface waters. *Journal of Chromatography A*, 1524, pp. 74-86.
- III Jakob Gustavsson*, Karin Wiberg, Erik Ribeli, Minh A. Nguyen, Sarah Josefsson, Lutz Ahrens (2017). Screening of organic flame retardants in Swedish rivers (submitted manuscript).
- IV Jakob Gustavsson*, Karin Wiberg, Minh A. Nguyen, Sarah Josefsson, Lutz Ahrens. Seasonal trends of flame retardants in river water in a boreal catchment (manuscript)

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The contribution of Jakob Gustavsson to the papers included in this thesis was as follows:

- I Planned the study together with the co-authors. Had main responsibility for laboratory experiments, laboratory analyses, data handling, data analyses, interpretations, writing and submission.
- II Planned the study together with the co-authors. Had main responsibility for laboratory experiments, laboratory analyses, data handling, data analyses, interpretations, writing and submission.
- III Planned the study together with the co-authors. Shared responsibility for sampling. Had main responsibility for laboratory analyses, data handling, data analyses, interpretations, writing and submission.
- IV Planned the study together with the co-authors. Had main responsibility for sampling, laboratory analyses, data handling, data analyses, interpretations and writing.

Abbreviations

Ac	Acetone
BEP	Brominated epoxyoligomer
Bp	Boiling point
BPS	Brominated polystyrene
CI-MS	Chemical ionization-mass spectrometry
COSMO	Conductor-like screening model
Cy	Cyclohexane
DCM	Dichloromethane
DOC	Dissolved organic carbon
EI-MS	Electron impact-mass spectrometry
EI-MS/MS	Electron impact-tandem mass spectrometry
FR	Flame retardant
GC	Gas chromatography
HCA	Hierarchical cluster analysis
HCB	Hexachlorobenzene
HFR	Halogenated flame retardant
HLB	Hydrophilic lipophilic balance
IDL	Instrumental detection limit
IS	Internal standard
KCS	Krycklan catchment study
KemI	Swedish Chemicals Agency
K_{OC}	Organic carbon-water partition coefficient
K_{OW}	Octanol-water partition coefficient
LC	Liquid chromatography
LOD	Limit-of-detection
LRAT	Long-range atmospheric transport
LRT	Long-range transport
LUMO	Lowest unoccupied molecular orbital
MDL	Method detection limit

ME	Matrix effect
MMI	Multimode inlet
SQL	Method quantification limit
MRM	Multiple reaction monitoring
MW	Molecular weight
NOM	Natural organic matter
OPFR	Organophosphorus flame retardant
oxy-PAH	Oxygenated-polycyclic aromatic hydrocarbon
PAH	Polycyclic aromatic hydrocarbon
PBB	Polybrominated biphenyl
PBDE	Polybrominated diphenyl ether
PCA	Principal component analysis
PCB	Polychlorinated biphenyl
PCDD/F	Polychlorinated dibenzo- <i>p</i> -dioxin/furan
PE	Petroleum ether
PFAS	Per- and polyfluorinated alkyl substance
POP	Persistent organic pollutant
SIM	Selective ion monitoring
SMHI	Swedish Meteorological and Hydrological Institute
SPE	Solid-phase extraction
SPM	Suspended particulate matter
TE	Total energy
TOC	Total organic carbon
US EPA	United States Environmental Protection Agency
WWTP	Waste water treatment plant

1 Introduction

1.1 A brief history of flame retardants

Flame retardants (FRs) are chemicals added to materials in order to provide fire protection. They can be either organic (carbon-based) or inorganic (metal salts etc.). Already in 450 BC, the Egyptians discovered that soaking wood in an aqueous solution of potassium aluminium sulphate ($\text{KAl}(\text{SO}_4)_2$) made the wood more difficult to burn (Cho, 2011). In 1638, theatre curtains in England were treated with a mixture of clay and gypsum ($\text{Ca}_2\text{SO}_4 \cdot 2 \text{H}_2\text{O}$) to increase their resistance to fire (Cho, 2011). The first patent of a FR was established in the United Kingdom in 1735 and consisted of a mixture of alum, vitriol and borax to be applied to textiles and paper pulp (Cho, 2011). Even though the use of FRs dates far back in history, it is only in recent decades that applications of FRs have expanded enormously (Guerra *et al.*, 2011). The development of new technology has led to increased use of synthetic polymers in many products used in *e.g.* residential homes, offices and public buildings (Guerra *et al.*, 2011, Alaei *et al.*, 2003). In today's modern society, FRs are extensively applied to combustible materials such as plastics, woods, paper and textiles (Guerra *et al.*, 2011), which are all common components of everyday products, such as furniture, carpeting, televisions, computers and building insulation (Barber *et al.*, 2012). According to industry estimates, the total annual consumption of FRs in Europe in 2006 was 465 000 metric tonnes (van der Veen & de Boer, 2012). However, the worldwide total consumption of FRs was in 2013 reported to be greater than 2 million tonnes, with the inorganic aluminium hydroxide being the single largest FR, corresponding to ~34% of the total volume (IHS consulting, 2014). The focus of this thesis is on organic FRs. Of these compound classes, halogenated FRs (HFRs), containing bromine and/or and chlorine, made up ~31% of total FR volume in 2013, while organophosphorus

FRs (OPFRs) corresponded to ~16% of the total volume (IHS consulting, 2014). Approximately, 85% of FR consumption is in the production of plastics, while rubber and textile products account for most of the rest (IHS consulting, 2014). Global consumption of FRs has been predicted to grow by 3.4% per year between 2013 and 2018 (IHS consulting, 2014). The increased use of FRs has led to a significant decrease in fire- and smoke-related fatalities (Birnbaum & Staskal, 2004), but FRs are also associated with environmental and human health concerns.

1.2 Why should we care about flame retardants?

Flame retardants have been a public concern ever since the polybrominated biphenyl (PBB) disaster in Michigan, US, in 1973. By accident, the feed constituent magnesium oxide was replaced by a FR formulation (marketed under the tradename Firemaster FF-1 by the Michigan chemicals company) during the production of cattle feed (Kay, 1977). The Firemaster FF-1 formulation consisted of a mixture of various PBBs, mainly hexabromo-biphenyl (Kay, 1977). The contamination of the cattle feed led to severe health effects on livestock and long-lasting exposure of Michigan inhabitants (Kay, 1977). Luckily, this type of extreme exposure to FRs is rare. Nevertheless, humans are exposed to a wide variety of chemicals (including, but not limited to, FRs) on a daily basis. FRs may be emitted to the environment during production, use and disposal of flame-amended products (Barber *et al.*, 2012). As these products (such as computers and furniture) surround people in their daily lives, this results in daily exposure via indoor air and dust. There are numerous studies analysing FRs in the indoor environment, both in indoor air (*e.g.* Marklund *et al.*, 2005, Green *et al.*, 2007, Schlabach *et al.*, 2011, Bergh *et al.*, 2011, Cequier *et al.*, 2014, Remberger *et al.*, 2014) and in dust (*e.g.* Van den Eede *et al.*, 2012, Remberger *et al.*, 2014, Abdallah & Covaci, 2014, He *et al.*, 2015, Brommer & Harrad, 2015, Luongo & Ostman, 2016). As an example, Cequier *et al.* (2014) investigated the occurrence of selected FRs in indoor air and dust from households and classrooms in Norway. Of the 37 FRs analysed, around 80% were detected in at least one sample, illustrating the wide range of FRs to which people are exposed in modern society. Human exposure to FRs is often found to be well below effect dose values (Ali *et al.*, 2012, Van den Eede *et al.*, 2012, Fromme *et al.*, 2014, Abdallah & Covaci, 2014), although contrasting findings have been reported (Luongo & Ostman, 2016). In addition to exposure via indoor air and dust, humans are probably also exposed to FRs via food and drinking water (EFSA, 2012), following the frequent detection of FRs in *e.g.* fish (Leonards *et al.*, 2011, Sundkvist *et al.*,

2010) and surface water (*e.g.* Andresen *et al.*, 2004, Cristale *et al.*, 2013). As a consequence, concerns have been raised about the potential risk associated with long-term exposure to FRs (Bergman *et al.*, 2012a). Human fetuses and toddlers are believed to be more sensitive than adults, especially during critical developmental stages (Bergman *et al.*, 2012a). This is particularly serious, since breastfeeding has been shown to provide the greatest lifetime exposure doses of polybrominated diphenyl ethers (PBDEs) of all life stages (Jones-Otazo *et al.*, 2005), which can be assumed to be valid also for many other FRs. In addition, toddlers are generally expected to be more exposed to dust than adults, due to their frequent hand-to-mouth contact and their ‘mouthing’ of objects, such as toys, that have been in contact with floors (Jones-Otazo *et al.*, 2005).

For many FRs, information about their potential toxic effects on humans is limited and this is particularly the case for newer FRs. However, for legacy FRs such as PBDEs, hexabromocyclododecane (HBCDD) and tetrabromobisphenol-A (TBBPA), toxicity studies exist. For those compounds, the main effects appear to be endocrine disruption, including oestrogenic and androgenic activity, alterations in receptor binding and disruption of thyroid hormones (Staskal Wikoff & Birnbaum, 2011, Darnerud, 2003, Birnbaum & Staskal, 2004, Vos *et al.*, 2003). Other observed effects include neurotoxicity, especially during development stages, and hepatotoxicity (Staskal Wikoff & Birnbaum, 2011, Birnbaum & Staskal, 2004). For PBBs, effects on reproduction, carcinogenicity, neurological and musculoskeletal symptoms have been suggested (Darnerud, 2003). Most OPFRs show strong haemolytic effects (decomposition of red blood cells) and some are possibly neurotoxic (van der Veen & de Boer, 2012). In addition, some OPFRs have been reported as affecting human reproduction, and chlorinated OPFRs have been shown to be carcinogenic (van der Veen & de Boer, 2012). Thus, minimising the exposure to these types of chemicals is important for human health.

Leakage of FRs from various products leads not only to their wide occurrence in the indoor environment, but also to their ubiquitous spread in the outdoor environment (de Wit *et al.*, 2010). In addition, many FRs have been predicted to be resistant to environmental degradation and to exhibit bioaccumulation potential (EFSA, 2012) and are suspected to be toxic to aquatic organisms (van der Veen & de Boer, 2012). Several FRs such as decabromodiphenylethane (DBDPE), hexabromobenzene (HBB) and pentabromoethylbenzene (PBEB) have been detected in polar bears (*Ursus maritimus*) in the Arctic, indicating long-range transport (LRT) and bioaccumulation (McKinney *et al.*, 2010). Another example is 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (EH-TBB), which has been detected in Arctic fox

(*Vulpes lagopus*) from the Norwegian Arctic (Sagerup *et al.*, 2010), also illustrating the wide spread of these type of organic pollutants in the global environment. Considering the ubiquitous distribution of FRs in the environment and their suspected adverse effects on organisms, it is imperative to monitor organic pollutants in the environment in order to prevent future disasters.

1.3 The chemistry of flame retardants

Flame retardants can be divided into additive, reactive or polymeric. Additive FRs are moulded into the material they aim to protect, without being chemically bound to it. Examples of additive FRs are PBBs, PBDEs, HBCDD, bis(2-ethylhexyl)tetrabromophthalate (BEH-TEBP), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), dibromoethyldibromocyclohexane (DBE-DBCH), DBDPE and tetrabromocyclooctane (TBCO) (Guerra *et al.*, 2011). In contrast to additive FRs, reactive FRs are chemically bound to the material they aim to protect, either by being incorporated into the polymer itself or by being covalently bond to the polymer backbone. Examples of reactive FRs are TBBPA, tetrabromophthalic anhydride (TEBP-Anh), 2,4,6-tribromophenol (TBP) and pentabromobenzylacrylate (PBB-Acr) (Guerra *et al.*, 2011). Lastly, in polymeric FRs bromine atoms are incorporated into the polymeric backbone. Two examples of polymeric FRs are brominated polystyrene (BPS) and brominated epoxy oligomers (BEP) (Guerra *et al.*, 2011). As a result of the chemical binding to the materials, reactive and polymeric FRs are less prone to leach from the finished products than additive FRs (de Wit *et al.*, 2010). However, unreacted FR may still be present in the products and may leak into the surrounding environment (de Wit *et al.*, 2010).

There are basically three different mechanisms for the mode of action of FRs in preventing fires: 1) gas-phase combustion inhibition, 2) endothermic decomposition and cooling of the fuel, and 3) condensed-phase char formation (Kirk-Othmer Encyclopedia of Chemical Technology, 2015). All FRs operate through one or several of those mechanisms. The HFRs and OPFRs are examples of FRs that act by inhibiting gas-phase combustion (mechanism 1). During a fire, the FR is volatilised and releases an active free-radical chemical species, such as a halogen or phosphorus radical (Kirk-Othmer Encyclopedia of Chemical Technology, 2015). During combustion, highly reactive radicals, which are essential for a fire to propagate, are formed within the flame (Arp *et al.*, 2010). However, when halogen or phosphorus radicals are formed within the flame, they react with the radicals of combustion and thereby interrupt the chain reactions that keep the fire going (Kirk-Othmer Encyclopedia of

Chemical Technology, 2015). Thus, fire development is quenched or at least slowed down. The mechanism of endothermic decomposition and cooling of the fuel (mechanism 2) is mainly exhibited by inorganic metal salts used as FRs, such as aluminium hydroxide and magnesium hydroxide (Kirk-Othmer Encyclopedia of Chemical Technology, 2015). Their flame-retarding properties are attributed to adsorption of heat when the metal salts decompose within a fire. This endothermic reaction cools the flame and thereby slows down the thermal decomposition and pyrolysis occurring in the flame (Kirk-Othmer Encyclopedia of Chemical Technology, 2015). In addition, some of these salts (*e.g.* metal hydroxides and carbonates) can release water or carbon dioxide when decomposing, which dilutes the fire fuel (Kirk-Othmer Encyclopedia of Chemical Technology, 2015). Moreover, non-flammable metal oxides can remain and dilute the fuel (Kirk-Othmer Encyclopedia of Chemical Technology, 2015). Lastly, the mechanism of condensed-phase char formation (mechanism 3) is exhibited by *e.g.* phosphorus- and nitrogen-containing FRs. Upon heating, this type of FR reacts with the fuel itself, forming a more thermally stable ‘char’. This char can still burn, but with lower intensity and heat release, which slows down fire development (Kirk-Othmer Encyclopedia of Chemical Technology, 2015).

1.4 Legacy flame retardants

Legacy FRs are compounds that have been extensively used as FRs in the past, but are no longer being used to the same extent for various reasons, such as legislative restrictions or voluntary phase-out. The PBDEs and PBBs are examples of legacy FRs and are discussed briefly in the following section. HBCDD and TBBPA are sometimes also classified as legacy FRs, but in this thesis are classified as alternative FRs (alternatives to PBDEs), despite their long historical use. A total of 27 legacy FRs (all PBDEs) were analysed in at least one of Papers I-IV in this thesis (Table 1).

1.4.1 PBDEs

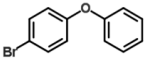
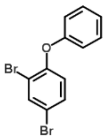
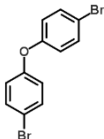
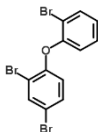
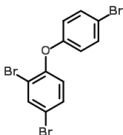
The structure of diphenyl ether contains 10 hydrogen atoms. Any of those hydrogens can be replaced with bromine, creating up to 209 possible congeners of brominated diphenyl ethers (BDEs) (Guerra *et al.*, 2011). In the past, BDEs (commonly known as PBDEs (poly-BDEs)) were extensively used as FRs, but are now banned as a consequence of their hazardous properties (Stapleton *et al.*, 2012). Basically, three commercial mixtures of PBDEs have been used: penta-, octa- and deca-BDE (Guerra *et al.*, 2011). Penta-BDE typically

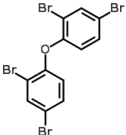
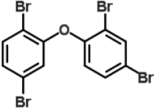
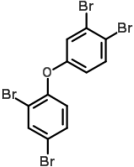
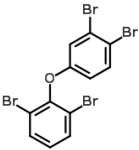
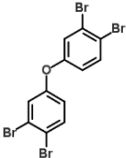
consisted of mainly tetra- (24-37%) and penta-brominated BDEs (50-60%), while the octa-BDE mixture typically contained mainly hepta- (44%) and octa-brominated (31-35%) BDEs. The deca-BDE formulation contained almost exclusively (>97%) deca-BDE (*i.e.* BDE209) (Guerra *et al.*, 2011). Tetra- to hepta-BDEs are included in the Stockholm Convention, and the use of penta- and octa-BDE has been banned in new materials in the European Union (EU) since 2009 (URL1). Deca-BDE is banned from use in electrical and electronic appliances within the EU (ECJ, 2008) and has recently been included in the Stockholm Convention (URL1).

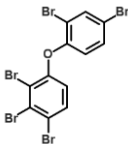
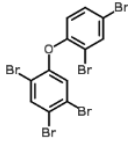
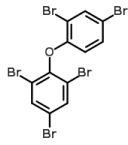
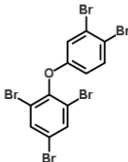
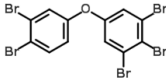
1.4.2 PBBs

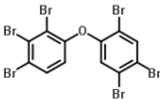
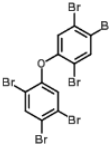
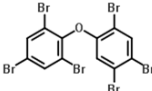
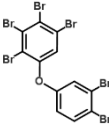
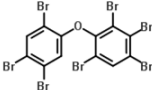
Similarly to PBDEs, there are 209 possible congeners of polybrominated biphenyls (PBBs). However, the commercial mixture consists mainly of hexa- to deca-BBs (Guerra *et al.*, 2011). PBBs were mainly produced in the early 1970s and were responsible for the contamination disaster in Michigan in 1973 (Kay, 1977). Shortly after this disaster, the production of hexabromobiphenyl ceased in the US, while the production of octa- and deca-BBs continued until 1977 (Guerra *et al.*, 2011). In Europe, PBBs have been restricted from use in textiles intended to come into contact with skin since 1984, and in 2000 the industry voluntarily ceased production of PBBs (Guerra *et al.*, 2011). Hexabromobiphenyl is included in the Stockholm Convention since 2009 (URL1).

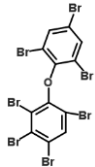
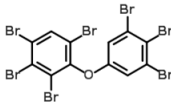
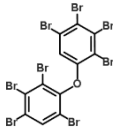
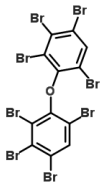
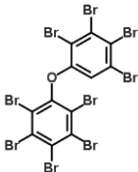
Table 1. Polybrominated diphenyl ethers (PBDEs, $n = 27$) analysed in this thesis

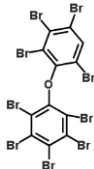
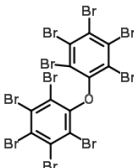
Abbreviation	Name	Structure ^a	Molecular formula	CAS no.
BDE3	4-Bromodiphenyl ether		$C_{12}H_9BrO$	101-55-3
BDE7	2,4-Dibromodiphenyl ether		$C_{12}H_8Br_2O$	147217-71-8
BDE15	Di(4-bromophenyl) ether		$C_{12}H_8Br_2O$	2050-47-7
BDE17	2,2',4-Tribromodiphenyl ether		$C_{12}H_7Br_3O$	147217-75-2
BDE28	2,4,4'-Tribromophenyl ether		$C_{12}H_7Br_3O$	41318-75-6

BDE47	2,2',4,4'- Tetrabromodiphenyl ether		$C_{12}H_6Br_4O$	5436-43-1
BDE49	2,2',4,5'- Tetrabromodiphenyl ether		$C_{12}H_6Br_4O$	243982-82-3
BDE66	2,3',4,4'- Tetrabromodiphenyl ether		$C_{12}H_6Br_4O$	189084-61-5
BDE71	2,3',4',6- Tetrabromodiphenyl ether		$C_{12}H_6Br_4O$	189084-62-6
BDE77	3,3',4,4'- Tetrabromodiphenyl ether		$C_{12}H_6Br_4O$	93703-48-1

BDE85	2,2',3,4,4'- Pentabromodiphenyl ether		$C_{12}H_5Br_5O$	82346-21-0
BDE99	2,2',4,4',5'- Pentabromodiphenyl ether		$C_{12}H_5Br_5O$	32534-81-9
BDE100	2,2',4,4',6'- Pentabromodiphenyl ether		$C_{12}H_5Br_5O$	189084-64-8
BDE119	2,3',4,4',6'- Pentabromodiphenyl ether		$C_{12}H_5Br_5O$	189084-66-0
BDE126	3,3',4,4',5'- Pentabromodiphenyl ether		$C_{12}H_5Br_5O$	366791-32-4

BDE138	2,2',3,4,4',5'- Hexabromodiphenyl ether		$C_{12}H_5Br_5O$	182677-30-1
BDE153	2,2',4,4',5,5'- Hexabromodiphenyl ether		$C_{12}H_4Br_6O$	68631-49-2
BDE154	2,2',4,4',5,6'- Hexabromodiphenyl ether		$C_{12}H_4Br_6O$	207122-15-4
BDE156	2,3,3',4,4',5- Hexabromodiphenyl ether		$C_{12}H_4Br_6O$	405237-85-6
BDE183	2,2',3,4,4',5',6- Heptabromodiphenyl ether		$C_{12}H_3Br_7O$	207122-16-5

BDE184	2,2',3,4,4',6,6'- Heptabromodiphenyl ether		$C_{12}H_3Br_7O$	117948-63-7
BDE191	2,3,3',4,4',5',6'- Heptabromodiphenyl ether		$C_{12}H_3Br_7O$	446255-30-7
BDE196	2,2',3,3',4,4',5,6'- Octabromodiphenyl ether		$C_{12}H_2Br_8O$	32536-52-0
BDE197	2,2'3,3',4,4',6,6'- Octabromodiphenyl ether		$C_{12}H_2Br_8O$	117964-21-3
BDE206	2,2',3,3',4,4',5,5',6'- Nonabromodiphenyl ether		$C_{12}HBr_9O$	63936-56-1

BDE207	2,2',3,3',4,4',5,6,6'- Nonabromodiphenyl ether		C ₁₂ HBr ₉ O	437701-79-6
BDE209	Decabromodiphenyl ether		C ₁₂ Br ₁₀ O	109945-70-2

^aStructures adopted from Chemspider chemical structure database

1.5 Alternative flame retardants

1.5.1 HBCDD

Hexabromocyclododecane (HBCDD) is included in the Stockholm Convention since 2013 (URL1). In 1999 and 2001, HBCDD was the second most used brominated FR in Europe (Guerra *et al.*, 2011). Theoretically, there are 16 different stereoisomers of HBCDD, but commercial products are typically a mixture of three diastereomers: α -, β - and γ -isomer, of which γ -isomer is the main isomer in commercial mixtures (75-89%) (Guerra *et al.*, 2011).

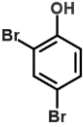
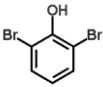
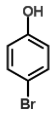
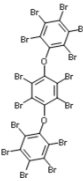
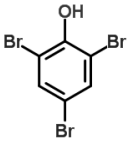
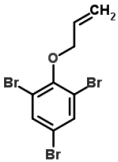
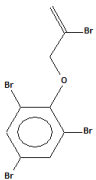
1.5.2 TBBPA

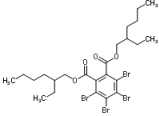
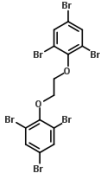
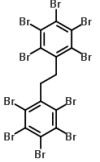
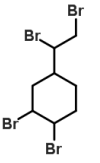
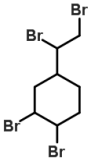
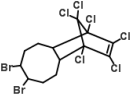
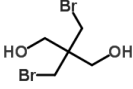
Tetrabromobisphenol-A (TBBPA) is mainly used as a reactive FR, but has also additive applications (Guerra *et al.*, 2011) and is often used in electrical and electronic equipment, such as computers and mobile phones (de Wit *et al.*, 2010). TBBPA is often listed as a legacy FR, but is likely to still be extensively used, as there are no restrictions on this compound. In 2011, TBBPA was reported to be the most used FR worldwide (Schlabach *et al.*, 2011).

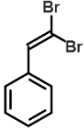
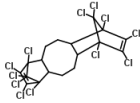
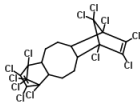
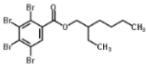
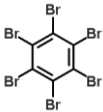
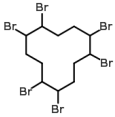
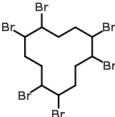
1.5.3 Other alternative flame retardants

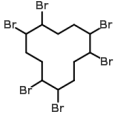
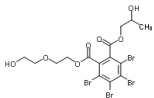
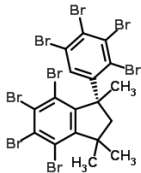
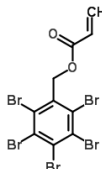
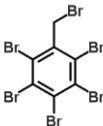
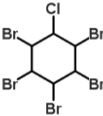
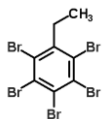
As a consequence of the restrictions on many legacy FRs, the need for alternatives in order to comply with current fire safety legislation has increased (Stapleton *et al.*, 2008, Stapleton *et al.*, 2012). This has led to the introduction of a large number of new/alternative FRs, often referred to as emerging FRs, on the global market (Bergman *et al.*, 2012b). The alternative FRs can be divided in two major groups based on their structure: HFRs, containing bromine or chlorine (or both), and OPFRs, containing one or several phosphate groups. However, some OPFRs (*e.g.* tri(1-chloro-2-propyl) phosphate (TCIPP), tris(1,3-dichloro-isopropyl) phosphate (TDCIPP) and tris(tribromoneopentyl) phosphate (TTBNPP)) also contain bromine/chlorine, but for simplicity are classified as OPFRs throughout this thesis. Despite the good intention of replacing hazardous legacy FRs with alternatives, it has been shown that many of the alternative FRs (*e.g.* BTBPE, pentabromotoluene (PBT), HBB and 2,3,5,6-tetrabromo-*p*-xylene (TBX)) have similar physicochemical properties to the legacy FRs (Liagkouridis *et al.*, 2015). In fact, a number of the alternative FRs have been detected in the environment, including *e.g.* BTBPE, HBB, DBE-DBCH and PBT in Arctic biota (Muir & de Wit, 2010, de Wit *et al.*, 2010), tributyl phosphate (TNBP), tris(2-chloroethyl) phosphate (TCEP) and TCIPP in waste and surface water (Gans *et al.*, 2007) and HBB, PBT and EH-TBB in sediment (Schlabach *et al.*, 2011). To date, analytical methods originally developed for legacy FRs have been employed for the analysis of alternative FRs (Covaci *et al.*, 2011). However, such methods are not optimised for these compounds, and thus there is a need for new analytical methods developed specifically for the alternative, non-legacy FRs, in order to obtain accurate and reliable data on their occurrence and levels in the environment. The development of new methods for the alternative FRs is one of the major aims of this thesis. Within this thesis work, a total of 46 HFRs (Table 2) and 29 OPFRs (Table 3) were analysed in at least one of Papers I-IV.

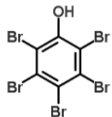
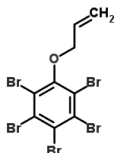
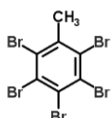
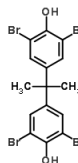
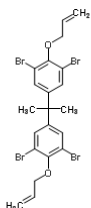
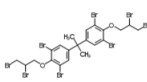
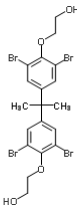
Table 2. Halogenated flame retardants (HFRs, $n = 46$) analysed in this thesis

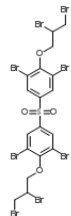
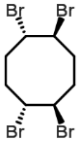
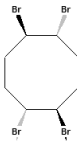

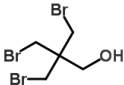
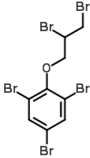
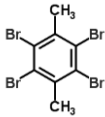
Abbreviation	Name	Structure ^a	Molecular formula	CAS no.
2,4-DBP	2,4-Dibromophenol		$C_6H_4Br_2O$	615-58-7
2,6-DBP	2,6-Dibromophenol		$C_6H_4Br_2O$	608-33-3
4-BP	4-Bromophenol		C_6H_5BrO	106-41-2
4'-PeBPO-BDE208	Pentabromophenoxy-nonabromo-diphenyl ether		$C_{18}Br_{14}O_2$	58965-66-5
TBP (2,4,6-TBP)	2,4,6-Tribromophenol		$C_6H_3Br_3O$	118-79-6
TBP-AE (ATE)	Allyl 2,4,6-tribromophenyl ether		$C_9H_7Br_3O$	221-913-2
BATE	2-Bromoallyl 2,4,6-tribromophenyl ether		$C_9H_6Br_4O$	na

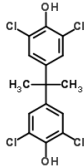
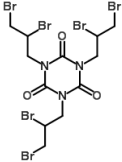
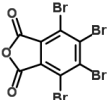
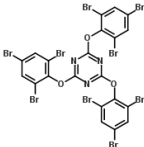
BEH-TEBP	Bis(2-ethyl-1-hexyl)- tetrabromo phthalate		$C_{24}H_{34}Br_4O_4$	26040-51-7
BTBPE	1,2-Bis(2,4,6- tribromophenoxy) ethane		$C_{14}H_8Br_6O_2$	37853-59-1
DBDPE	1,2-Bis(2,3,4,5,6- pentabromophenyl) ethane		$C_{14}H_4Br_{10}$	84852-53-9
α -DBE-DBCH (TBECH)	1,2-Dibromo-4-(1,2- dibromoethyl) cyclohexane		$C_8H_{12}Br_4$	3322-93-8
β -DBE-DBCH (TBECH)	1,2-Dibromo-4-(1,2- dibromoethyl) cyclohexane		$C_8H_{12}Br_4$	3322-93-8
DBHCTD	Hexachlorocyclo- pentadienyl dibromocyclooctane		$C_{13}H_{12}Br_2Cl_6$	51936-55-1
DBNPG	Dibromo- neopentyl alcohol		$C_5H_{10}Br_2O_2$	3296-90-0

DBS	(2,2-Dibromovinyl) benzene		$C_8H_6Br_2$	31780-26-4
anti-DDC-CO (anti-DP)	Dechlorane Plus		$C_{18}H_{12}Cl_{12}$	13560-89-9
syn-DDC-CO (syn-DP)	Dechlorane Plus		$C_{18}H_{12}Cl_{12}$	13560-89-9
EH-TBB	2-Ethylhexyl 2,3,4,5-tetrabromobenzoate		$C_{15}H_{18}Br_4O_2$	183658-27-7
HBB	Hexabromo-benzene		C_6Br_6	87-82-1
α -HBCDD	Hexabromo-cyclododecane		$C_{12}H_{18}Br_6$	3194-55-6
β -HBCDD	Hexabromo-cyclododecane		$C_{12}H_{18}Br_6$	3194-55-6

γ -HBCDD	Hexabromo- cyclododecane		$C_{12}H_{18}Br_6$	3194-55-6
HEEHP-TEBP	2-(2-Hydroxyethoxy)- ethyl-2-hydroxy-propyl- 3,4,5,6- tetrabromophthalate		$C_{15}H_{16}Br_4O_7$	20566-35-2
OBTMPI	4,5,6,7-Tetrabromo- 1,1,3- trimethyl-3-(2,3,4,5- tetrabromophenyl)- indane		$C_{18}H_{12}Br_8$	1084889-51-9
PBB-Acr	Pentabromobenzyl acrylate		$C_{10}H_5Br_5O_2$	59447-55-1
PBBB (PBBBr)	Pentabromobenzyl- bromide		$C_7H_2Br_6$	38521-51-6
PBCH	Pentabromochloro- cyclohexane		$C_6H_6Br_5Cl$	87-84-3
PBEB	Pentabromoethyl- benzene		$C_8H_5Br_5$	85-22-3

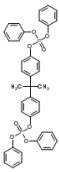
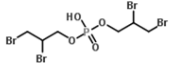
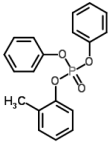
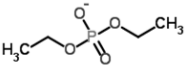
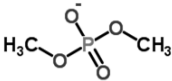
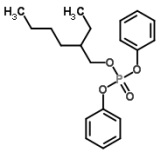
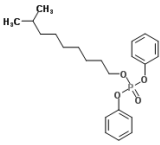
PBP	Pentabromo-phenol		C_6Br_5OH	608-71-9
PBPAE	Pentabromo-phenyl allyl ether		$C_9H_5Br_5O$	3555-11-1
PBT	Pentabromo-toluene		$C_7H_3Br_5$	87-83-2
TBBPA	Tetrabromo-bisphenol A		$C_{15}H_{12}Br_4O_2$	79-94-7
TBBPA-BAE	Tetrabromo-bisphenol A bis(allyl ether)		$C_{21}H_{20}Br_4O_2$	25327-89-3
TBBPA-BDBPE	Tetrabromo-bisphenol A-bis(2,3-dibromopropyl ether)		$C_{21}H_{20}Br_8O_2$	21850-44-2
TBBPA-DHEE	Tetrabromo-bisphenol A dihydroxyethyl ether		$C_{19}H_{20}Br_4O_4$	4162-45-2

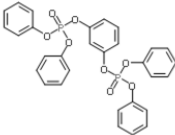
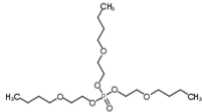
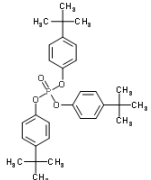
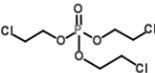
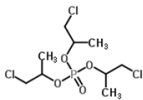
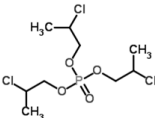
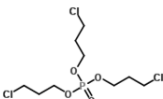
TBBP-DBPE	Tetrabromo-bisphenol-S-bis-(2,3-dibromopropyl) ether		$C_{18}H_{14}Br_8O_4S$	42757-55-1
α -TBCO	(1R,2R,5S,6S)-1,2,5,6-Tetrabromo-cyclooctane		$C_8H_{12}Br_4$	3194-57-8
β -TBCO	rac-(1R,2R,5R,6R)-1,2,5,6-Tetrabromo-cyclooctane		$C_8H_{12}Br_4$	3194-57-8
TBCT	1,2,3,4-Tetrabromo-5-chloro-6-methylbenzene		$C_7H_3Br_4Cl$	39569-21-6
TBNPA	Tribromoneopentyl alcohol		$C_5H_9Br_3O$	1522-92-5
TBP-DBPE	2,3-Dibromopropyl-2,4,6-tribromophenyl ether		$C_9H_7Br_5O$	35109-60-5
TBX	2,3,5,6-Tetrabromo-p-xylene		$C_8H_6Br_4$	23488-38-2

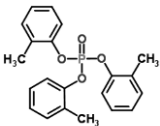
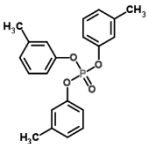
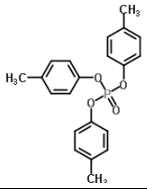
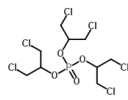
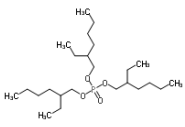
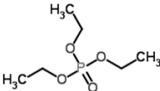
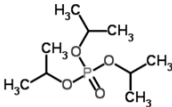
TCBPA	Tetrachloro-bisphenol-A		$C_{15}H_{12}Cl_4O_2$	27360-90-3
TDBP-TAZTO	1,3,5-Tris(2,3-dibromopropyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione		$C_{12}H_{15}Br_6N_3O_3$	52434-90-9
TEBP-Anh	3,4,5,6-Tetrabromophthalic anhydride		$C_8Br_4O_3$	632-79-1
TTBP-TAZ	2,4,6-Tris(2,4,6-tribromophenoxy)-1,3,5-triazine		$C_{21}H_6Br_9N_3O_3$	25713-60-4

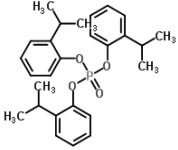
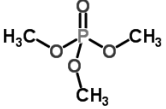
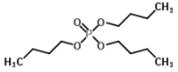
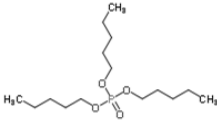
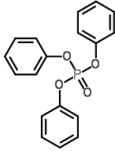

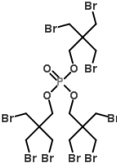
^aStructures adopted from Chemspider chemical structure database, except BATE and β -TBCO which were manually drawn in EPIsuite 4.1 (US EPA)

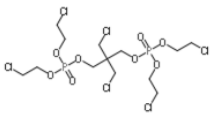
Table 3. Organophosphorus flame retardants (OPFRs, $n = 29$) analysed in this thesis

Abbreviation	Name	Structure ^a	Molecular formula	CAS no.
BADP	Bisphenol A bis (diphenyl phosphate)		$C_{39}H_{34}O_8P_2$	5945-33-5
bBDBP	Bis(2,3-dibromopropyl) phosphate		$C_6H_{11}Br_4O_4P$	5412-25-9
CDP	Cresyl diphenyl phosphate		$C_{19}H_{17}O_4P$	26444-49-5
mDEP/ dDEP	Diethyl phosphate (mono/di)		$C_4H_{11}O_4P$	598-02-7
DMP	Dimethyl phosphate		$C_2H_7O_4P$	813-78-5
EHDPP	2-Ethylhexyl diphenyl phosphate		$C_{20}H_{27}O_4P$	1241-94-7
IDP	Isodecyl diphenyl phosphate		$C_{22}H_{31}O_4P$	29761-21-5

PBDPP (RDP)	Resorcinol bis (diphenyl phosphate)		$C_{30}H_{24}O_8P_2$	57583-54-7
TBOEP	Tri(2-butoxyethyl) phosphate		$C_{18}H_{39}O_7P$	78-51-3
TBPP	Tris(4-tert- butylphenyl) phosphate		$C_{30}H_{39}O_4P$	78-33-1
TCEP	Tris(2-chloroethyl) phosphate		$C_6H_{12}Cl_3O_4P$	115-96-8
TCIPP	Tri(1-chloro-2- propyl) phosphate		$C_9H_{18}Cl_3O_4P$	13674-84-5
T2CPP	Tri(2-chloropropyl) phosphate		$C_9H_{18}Cl_3O_4P$	6145-73-9
T3CPP	Tri(3-chloropropyl) phosphate		$C_9H_{18}Cl_3O_4P$	26248-87-3

<i>o</i> -TMPP (<i>o</i> -TCP)	<i>ortho</i> -Tritolyl phosphate		C ₂₁ H ₂₁ O ₄ P	1330-78-5
<i>m</i> -TMPP (<i>m</i> -TCP)	<i>meta</i> -Tritolyl phosphate		C ₂₁ H ₂₁ O ₄ P	1330-78-5
<i>p</i> -TMPP (<i>p</i> -TCP)	<i>para</i> -Tritolyl phosphate		C ₂₁ H ₂₁ O ₄ P	1330-78-5
TDCIPP	Tris(1,3-dichloro- isopropyl) phosphate		C ₉ H ₁₅ Cl ₆ O ₄ P	13674-87-8
TEHP	Tris(2-ethylhexyl) phosphate		C ₂₄ H ₅₁ O ₄ P	78-42-2
TEP	Triethyl phosphate		C ₆ H ₁₅ O ₄ P	78-40-0
TiPP	Triisopropyl phosphate		C ₉ H ₂₁ O ₄ P	513-02-0

TiPPP	Tri(2-Isopropyl-phenyl) phosphate		$C_{27}H_{33}O_4P$	64532-95-2
TMP	Trimethyl phosphate		$C_3H_9O_4P$	512-56-1
TNBP	Tributyl phosphate		$C_{12}H_{27}O_4P$	126-73-8
TPeP	Triphenyl phosphate		$C_{15}H_{33}O_4P$	2528-38-3
TPHP	Triphenyl phosphate		$C_{18}H_{15}O_4P$	115-86-6
TPP	Tripropyl phosphate		$C_9H_{21}O_4P$	513-08-6
TTBNPP	Tris(tribromo-neopentyl) phosphate		$C_{15}H_{24}Br_9O_4P$	19186-97-1

V6	Tetrakis(2-chloroethyl) dichloroisopentyl diphosphate		$C_{13}H_{24}Cl_6O_8P_2$	38051-10-4
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^aStructures adopted from Chemspider chemical structure database

2 Overall aim of the thesis and objectives of Papers I-IV

The overall aim of this thesis was to develop an analytical method for the analysis of alternative FRs. A further aim was to assess the current level of FR pollution in Sweden and to improve understanding of transport and fate for FRs within pristine and polluted boreal catchments, including the impact of various sources of contamination and environmental pathways. Specific objectives for each individual paper (Paper I-IV) are described below.

Paper I

The objectives of Paper I were to compare three mass spectrometry (MS) techniques for the analysis of FRs, to investigate the influence of matrix on instrumental analysis of FRs, and to test the potential of three different sorbents for clean-up of freshwater samples containing FRs.

Paper II

The objectives of Paper II were to evaluate five sorbents for extraction of FRs from natural water, to investigate the influence of dissolved natural organic matter (NOM) on the extraction efficiency of FRs from water and to increase understanding of how different properties of FRs affect the relative influence of dissolved NOM on extraction efficiency and the mechanisms behind the observed effects.

Paper III

The main objectives of Paper III were to identify potential point sources and source pathways of FRs in the Swedish environment, to correlate FR levels to environmental variables, and to estimate daily fluxes of FRs from Swedish rivers into the Baltic Sea.

Paper IV

The main objectives of Paper IV were to investigate the influence of seasonality and land-cover type for surface water concentrations and transport of FRs within a boreal catchment and to determine the relative importance of remote boreal catchments for FR concentrations compared with point sources located further downstream.

3 Methods

The work upon which this thesis is built was divided into two parts. The first part (Papers I and II) involved the development of analytical methodology for analysis of flame retardants (FRs), comprising solid-phase extraction (SPE) (Paper II), clean-up (Paper I) and instrumental analysis (Paper I). As part of method development, different analytical challenges were investigated, including matrix effects during instrumental analysis (Paper I) and the influence of NOM on SPE extraction efficiency (Paper II). The second part (Papers III and IV) involved assessing the current situation of FR pollution in Sweden, with emphasis on Swedish rivers (Paper III) and a relatively pristine boreal catchment (Paper IV). During this work, potential point sources were sought for the Swedish rivers and the influence of seasonal variations on FR concentrations was investigated. A flow chart of the analytical protocol used within this thesis is given in Figure 1.

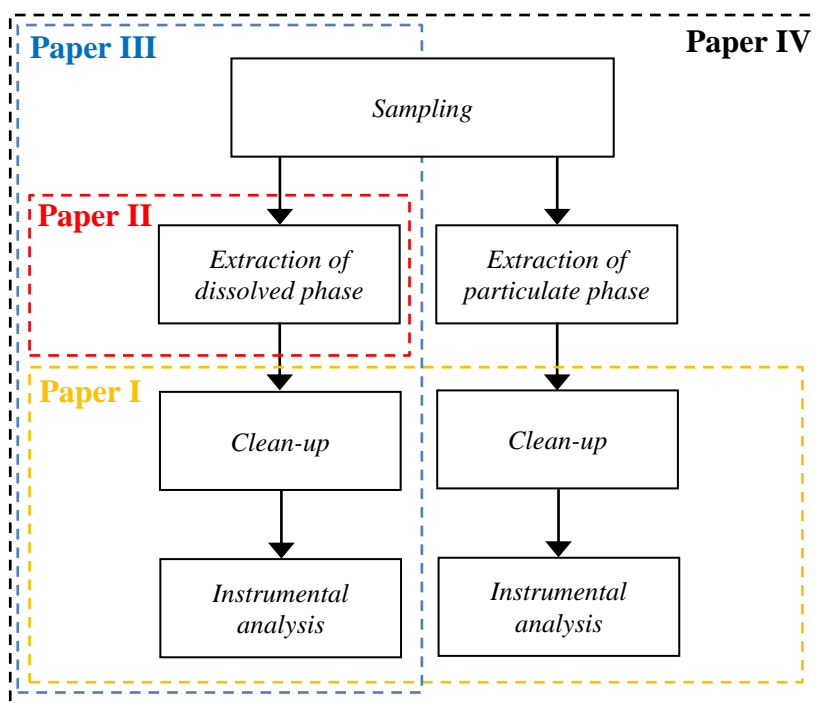


Figure 1. Flow chart illustrating the analytical protocol used in each of Papers I-IV.

Sampling

Papers I and II focused on analytical method development for FRs and therefore only a few samples were collected, while Papers III and IV were based on field studies and included a number of sampling campaigns. For Paper III, a sampling campaign was undertaken in October 2013 (for details, see Paper III). Bulk surface water samples (10 L) were collected from mainly river mouths ($n = 23$) all along the Swedish east coast ($n = 30$, including 2 blank samples), from Haparanda in the north (latitude 66°N) to Kristianstad in the south (latitude 56°N). Sampling locations and river names are presented in Figure 2. River water was collected by suspending a stainless steel bucket attached to a 30 m rope from a bridge in the middle of each river or, where no bridge was available, from the shore. The sampled water was transferred to a stainless steel container and was stored at +4 °C until extraction.

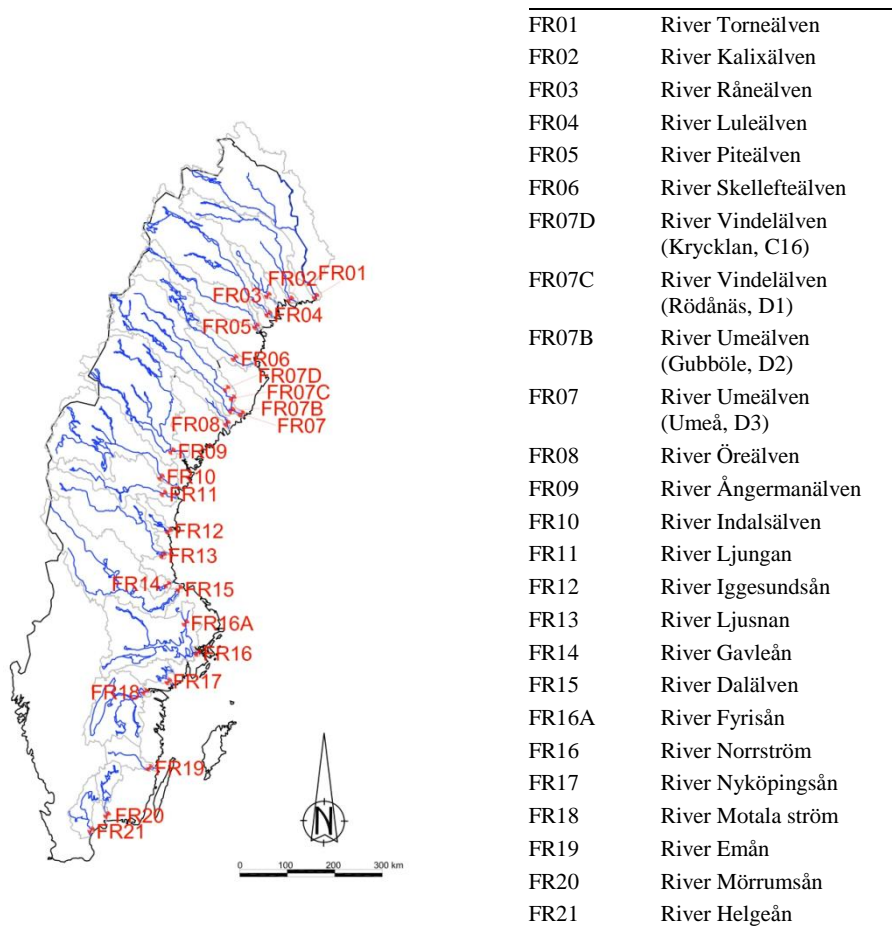


Figure 2. Sampling locations with sample ID code and river name, sorted from north (top) to south (bottom) of Sweden. Source: Paper III.

In Paper IV, water samples were collected within the Krycklan Catchment Study (KCS) area and further downstream along a gradient of increased human impact towards the Gulf of Bothnia (northernmost part of the Baltic Sea, Figure 3). Stream water samples were collected over a period of approximately two years (October 2014 to June 2016, $n = 76$, including 8 blank samples), covering three hydrological seasons, *i.e.* snow-free season, snow-covered season and spring flood (for details, see Paper IV). Samples were collected at three sites within the KCS area (C2, C4 and C16) and three sites downstream

of the catchment (D1, D2 and D3). The downstream sampling sites (D1, D2 and D3) were the same sites as sampled in Paper III (Figure 2, referred to there as FR07C, FR07B and FR07, respectively). The sampled streams within the KCS area represent different land-cover types, where C2 is an entirely forested sub-catchment (100% forest; stream order 1), C4 is a sub-catchment with a relatively large proportion of mire (56% forest, 44% mire; stream order 1) and C16 is located at the outlet of the KCS catchment (stream order 4). Separate samples for determination of apparently dissolved FRs and FRs associated with the particulate fraction were collected. Particles were collected by pumping water in the field through glass fibre filters (GF/Fs, $0.7\ \mu\text{m}$), with a total of six filters per sample ($n = 76$, including 19 blank samples), representing water sample volumes between 70 and 1200 L. For analysis of the apparently dissolved phase, a fraction of the filtered water was collected in stainless steel containers (12 L) and brought to the laboratory. Water samples were stored at $+4^\circ\text{C}$ and filter samples were kept frozen (-18°C) until extraction.

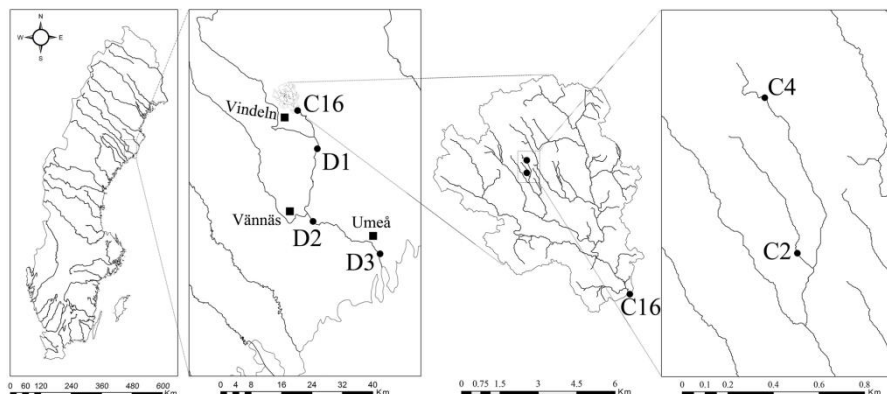


Figure 3. Locations of the six sampling sites (black dots ●) and nearby towns and cities (black squares ■) in a boreal catchment in northern Sweden (Krycklan Catchment Study area). Source: Nguyen *et al.*, (*in prep.*).

3.1 Extraction and elution

One of the aims of Paper II was to evaluate five different sorbents for extraction of FRs from natural water. The first step was to test different solvents for elution of FRs from each sorbent. This was done by spiking FRs ($n = 34$) directly onto each sorbent (*i.e.* XAD-2, IRA743, HR-P, HR-X and HLB) in duplicate and eluting with three different solvent mixtures (dichloromethane (DCM), acetone:cyclohexane (Ac:Cy) 1:1 (v/v) and Ac:Cy 1:4 (v/v)) (for details, see Paper II). The solvent/solvent mixture resulting in the

highest recovery for each sorbent was used for elution in the subsequent experiment, where the different sorbents were tested for their ability to trap FRs. This was done by spiking FRs ($n = 33$) directly onto each sorbent, followed by pumping pre-filtered (GF/F, $0.7\ \mu\text{m}$) surface river water ($\sim 11\ \text{L}$, collected from the Fyris River in central Uppsala, $\sim 5\ \text{km}$ upstream of site FR16A in Paper III) through the spiked sorbent. After elution with the selected solvent and further treatment, extracts were analysed and recoveries evaluated to find the most efficient sorbent for extracting FRs from water.

Another aim of Paper II was to investigate the influence of NOM on the extraction efficiency of FRs from water. This was done by conducting an experiment where artificial freshwater ($10\ \text{L}$) was fortified with different amounts of NOM ($0\text{--}60\ \text{mg L}^{-1}$) (for details, see Paper II). The artificial freshwater was also spiked with FRs ($n = 26$) and extracted using the optimal extraction sorbent (*i.e.* HLB) and elution solvent (*i.e.* DCM) identified in the previous experiments (Paper II). After further treatment of the extracts and instrumental analysis, recovery rates were determined. In order to better understand the relationship between FR properties and the impact of NOM on the extraction efficiency, physicochemical properties and semi-empirical quantum chemistry properties were modelled using EPIsuite 4.1 (US EPA) and MOPAC2016 (Stewart Computational Chemistry), respectively. The modelled properties were then used in a principal component analysis (PCA) and a hierarchical cluster analysis (HCA), which were also used to interpret the results obtained in the NOM experiment (by dividing the FRs into groups).

In Paper III, water samples were extracted with SPE using Amberlite XAD-2 as the sorbent material. As discussed in Paper III, the analysed fraction represented the apparently dissolved phase. Glass columns filled with $20\ \text{g}$ of XAD-2 sorbent (pre-cleaned with Soxhlet extraction using methanol for $48\ \text{h}$, followed by ethyl acetate for $48\ \text{h}$) were used for extraction by pumping $\sim 10\ \text{L}$ water samples through the column. Prior to extraction, internal standards were added to the water samples. After extraction, any remaining water was removed by drying the column with nitrogen (N_2) gas. Elution was performed using two times $70\ \text{mL}$ of DCM. After water removal and solvent evaporation, the extracts were split into two equal aliquots, one of which was stored for potential future use, while the other was cleaned up using alumina according to the clean-up method developed in Paper I.

In Paper IV, after the addition of internal standards, extraction was conducted using Oasis HLB, as this was the sorbent with the highest overall recoveries in Paper II. After loading the cartridge with the $10\text{--}12\ \text{L}$ water sample by applying negative pressure, SPE cartridges were centrifuged to remove excess water. DCM ($50\ \text{mL}$) was found to be the optimal elution

solvent for FRs from the HLB sorbent and was therefore used to rinse the sample containers and subsequently also for elution of the cartridges. This rinsing/elution step was repeated three times. Prior to each rinsing of the sample container and elution, the inner wall of the SPE cartridge was rinsed with ~10 mL DCM. Thus, total elution volume was 180 mL.

Filter samples collected in Paper IV (corresponding to 70-1200 L of water, 0.20-280 mg SPM L⁻¹) were extracted using Dean-Stark Soxhlet extraction with toluene for 24 hours. Prior to extraction, internal standards were spiked directly onto the filters placed in the Soxhlet. All six filters from each site were extracted together.

3.2 Sample clean-up

In Paper I, three different sorbents (Florisil[®], acidified silica and alumina) were compared for their suitability for clean-up of surface water extracts containing FRs ($n = 30$). Surface water extracts ($n = 4$) were prepared from Fyris River water (site FR16A in Paper III, Uppsala, Sweden). The four river extracts were combined, thoroughly mixed and split into 13 equal aliquots. Two extracts for each clean-up sorbent (duplicates) were spiked with FRs, while two extracts for each clean-up sorbent remained unspiked (Figure 4). However, one of the two unspiked extracts was spiked after clean-up, to serve as a matrix-matched reference. For comparison, one extract was spiked but not cleaned up. The resulting recoveries were evaluated and the superior clean-up method was then used for clean-up of sample extracts in Papers III and IV. This method was based on alumina (1 g, 6% deactivation), using a 95/5 (v/v) mixture of petroleum ether (PE)/DCM for conditioning and elution (for details, see Paper I).

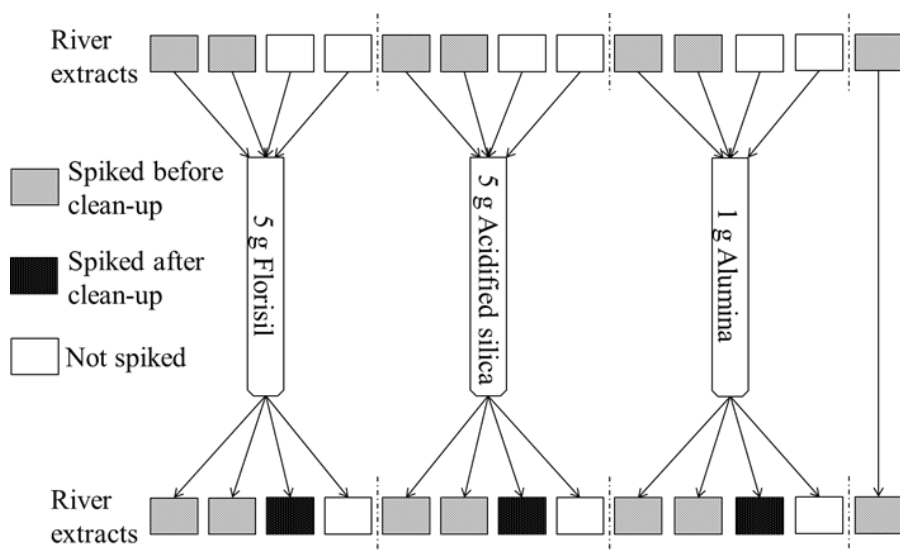


Figure 4. Schematic diagram of the clean-up experiment. Source: Paper I.

3.3 Instrumental analysis

In Paper I, instrumental methods were developed using three types of instrumental set-ups based on gas chromatography (GC) coupled to mass spectrometry (MS) with electron impact (EI) and negative chemical ionisation (NCI), *i.e.* GC-(EI)MS/MS, GC-(EI)MS and GC-(NCI)MS (for details, see Paper I). Each FR ($n = 102$) was injected individually into each MS system operating in SCAN mode. Based on the resulting mass spectra, two (if available) mass fragments for each FR were selected and used to create selective ion monitoring (SIM) methods for the two single MS instruments. In the tandem mass spectrometer, the selected fragments were used to create a product ion scan method. With this type of method, the first quadrupole is set to let only the selected fragments (precursor ions) pass through the quadrupole into the collision cell, where those fragments are further fragmented to product ions. The product ions are then scanned by the second quadrupole to determine what product ions each precursor ion generates when further fragmented in the collision cell. This information was used in Paper I to create a multiple reaction monitoring (MRM) method for the tandem instrument. Finally, the collision energies applied in the collision cell were optimised for each individual FR by applying different collision energies and observing the resulting peak intensities. In parallel with this work, GC parameters were optimised. Details of the selected MS and GC parameters are given in Paper I.

After the instrumental methods had been developed, the three instrumental systems were compared in terms of their ability to detect FRs in ultra-trace concentrations, *i.e.* their instrumental detection limit (IDLs) (details in Paper I). For this purpose, a water extract was prepared from Fyris River water (site FR16A in Paper III, Uppsala, Sweden). The extract was divided into three equal aliquots. Two of the aliquots were spiked with selected FRs ($n = 45$), at a concentration close to the limit of detection (LOD) and at 10 times LOD, respectively. The third aliquot was not spiked and was used for correction of background levels of FRs. Each of the extracts corresponded to 4 L of river water. Finally, the solvent was exchanged to toluene with a final volume of 100 μ L. Each extract was injected five consecutive times on each of the three instrumental systems, operating in SIM (single MS) and MRM (tandem MS) mode. The IDL was calculated using the following formula: $IDL = (stdev \cdot t_{\alpha} \cdot c) / \text{mean}$, where *stdev* is the standard deviation of the peak area ($n = 5$), t_{α} is the student's *t*-value (one-sided, 95%-confidence interval, degrees-of-freedom = 4), *c* is the spiked concentration, and *mean* is the calculated mean of the peak area after background correction ($n = 5$). Based on the IDLs obtained, GC-(EI)MS/MS was selected for use for the instrumental analysis in Papers III and IV.

Matrix effects were evaluated in Paper I by comparing the instrumental response of a spiked extract (an aliquot of the previously prepared Fyris River extract) with a pure solvent standard spiked with the same FR concentrations as the river extract (~10 times LOD). The spiked river extract, an unspiked river extract and the spiked solvent standard were analysed using GC-(EI)MS, as this was assumed to be the instrumental system most sensitive to matrix effects. The matrix effects were evaluated using the following formula: $\text{Matrix effect} = (R_{SE} - R_{BLK}) / R_{SS}$, where R_{SE} is the response of the spiked river water extract, R_{BLK} is the response of the blank extract and R_{SS} is the response of the spiked solvent standard.

3.4 Quality assurance and quality control

Isotopically labelled internal standards (ISs) were added to samples prior to extraction and used to correct for losses occurring during the analytical procedures in Papers I, III and IV (use of ISs was not necessary in Paper II). For many alternative FRs, corresponding isotopically labelled ISs are not available, and therefore surrogate ISs were selected for most of those FRs. This was done by slightly different approaches in the different papers. In Paper I, $^{13}\text{C}_{12}$ -BDE139 was used for all PBDEs, $^{13}\text{C}_6$ -HBB for all HFRs and d_{15} -TPHP for all OPFRs, while three isotopically labelled BDEs were used for all FRs in

Paper III, assigned to each FR based on retention time. In Paper IV, the ISs used were selected based on the behaviour of the different FRs during extraction in response to increasing NOM concentrations in Paper II (*i.e.* $^{13}\text{C}_{12}$ -BDE79 was used for all PBDEs, $^{13}\text{C}_6$ -HBB for all HFRs except dechlorane plus (DDC-CO), $^{13}\text{C}_{10}$ -DDC-CO for DDC-CO and d_{27} -TNBP for all OPFRs).

In order to reduce the potential background contamination during sample collection and laboratory work, all sampling equipment, tools and laboratory glassware that came into direct contact with the sample were cleaned in a laboratory dishwasher, incinerated (400°C, if possible) and rinsed with organic solvent before use. Sample containers were rinsed with hot water, distilled water, 0.1 M hydrochloric acid, acetone and Millipore water prior to sampling. In the field, buckets and sample containers were rinsed three times with river water before the sample was collected. In Papers III and IV, laboratory and field blanks were extracted and analysed in parallel with samples to check for potential background contamination. If a target FR was detected in the blanks, the method detection limit (MDL) was calculated as the average of blanks plus three times the standard deviation (Papers III and IV). If a target FR was not detected in the blanks, the calculated IDL from Paper I was used as MDL, while if no IDL was available the lowest calibration point was used as MDL. In Paper III, the method quantification limit (MQL, above which concentrations are reported) was calculated as $\text{MDL}/3 \times 10$. In Paper IV, MDL was used as MQL.

All laboratory experiments conducted within this thesis were conducted using replicates (for details, see Papers I and II). During sampling, replicate samples were collected from at least one site (for details, see Papers III and IV).

4 Results and discussion

4.1 Analysis of flame retardants

4.1.1 Extraction of flame retardants from water (Paper II)

In Paper II, five different sorbents (XAD-2, IRA743, HR-P, HR-X and HLB) were evaluated for their efficiency in extracting FRs from natural water. First, three different elution solvents (DCM, Ac:Cy 1:1 and Ac:Cy 1:4) were evaluated for each sorbent. The results showed that the elution efficiency was highly dependent on the elution solvent and that the selected FRs ($n=34$) were most efficiently eluted using the solvent mixture Ac:Cy 1:4 (v/v) for XAD-2 and IRA743, and DCM for HR-P, HR-X and HLB. In the subsequent extraction experiment, it was found that the efficiency of extracting FRs from river water was as follows: HLB > XAD-2 >> IRA743 (HR-P and HR-X were excluded from the evaluation due to high background levels of polycyclic aromatic hydrocarbons (PAHs)). Based on these experiments, HLB as sorbent with DCM as the elution solvent was concluded to be the optimal combination for extraction of FRs from natural water.

The sorbent HLB was also used to investigate the influence of NOM on the extraction efficiency of FRs from water. It became evident during the experiments that NOM highly influenced the recovery of all FRs tested and that the recovery trends over the NOM gradient were linked to the properties of the FRs (Figure 5). The FRs were divided into four distinct groups using PCA and HCA, based on GC retention times and modelled values of physicochemical and semi-empirical quantum chemistry properties. These four groups were characterised by: i) high molecular weight (MW), high organic carbon-water partition coefficient (K_{OC}) and high lowest unoccupied molecular orbital (LUMO) energy (Group A), ii) low MW, low K_{OC} , low LUMO energy

and high dipole moment (Group B), iii) large conductor-like screening model (COSMO) area, high boiling point (Bp) and high total energy (TE) (Group C), and iv) large COSMO area, high Bp, high TE and large dipole moment (Group D). Three FRs (DDC-CO, tribromoneopentyl alcohol (TBNPA) and TDCIPP) could not be classified into any of the four groups due to deviating properties (see Figure 2 in Paper II).

The FRs in Group A showed decreasing recoveries until 20 mg NOM L⁻¹, followed by increasing recoveries up to 60 mg NOM L⁻¹. This indicates binding to sorbent-associated NOM at higher NOM levels. The FRs in Group B showed a slightly different recovery curve, with decreasing recoveries until 20 mg L⁻¹ NOM, then virtually no change up to 40 mg L⁻¹, and finally increasing recovery up to 60 mg L⁻¹. The recovery of two FRs (TBCO and DBE-DBCH) exceeded 100%, indicating matrix effects. In Group C, most FRs showed a similar recovery trend with increasing NOM concentrations, as also observed for Group A and for TBNPA. Moreover, BDE15 (the PBDE with the lowest MW) in Group B showed similar behaviour to this. In contrast, pentabromophenyl allyl ether (PBPAE) and PBB-Acr in Group C behaved differently, both showing values exceeding 100%, indicating matrix effects caused by NOM. These observations are in line with findings in Paper I, where both PBPAE and PBB-Acr showed matrix enhancement (section 4.1.3). The OPFRs in Group D (and also the ungrouped OPFR TDCIPP) showed highly variable recoveries, with decreases between 0 and 20 mg NOM L⁻¹, increases between 20-40 mg NOM L⁻¹, and again decreasing recoveries between 40 and 60 mg NOM L⁻¹. This clearly indicates that multiple counteracting mechanisms affect the recovery. A plausible explanation for the variable trend curve is that the sorbent adsorbs the NOM to which FRs bind. At higher NOM levels, the sorbent becomes saturated by NOM, in combination with an increase in elution strength of the water due the increased NOM concentration, leading to lower recoveries above 40 mg NOM L⁻¹ (for details, see Paper II). An alternative explanation for the decreasing recovery above 40 mg NOM L⁻¹ may be that the elution solvent is not strong enough to elute the complete NOM-sorbent layer, as this grows thicker with increasing NOM concentration.

Overall, the majority of the FRs in Groups A, B and C showed increasing recoveries between NOM levels of 20 and 40 mg L⁻¹, which might be attributable to binding of the FRs to a formed NOM-sorbent layer. However, the increase in recovery for those FRs was not as large as for PBB-Acr, TBNPA and OPFRs, which might be a result of stronger binding strength, *e.g.* from hydrogen bonds. The formation of strong hydrogen bonds is possibly a key feature of the interactions between NOM and PBB-Acr, TBNPA and OPFRs, which all contain moieties (=O or -OH) that can form strong hydrogen

bonds. The strong binding to the NOM-sorbent layer makes the extraction more efficient than when no NOM is present (NOM 0 mg L⁻¹), and thus recoveries can exceed 100%.

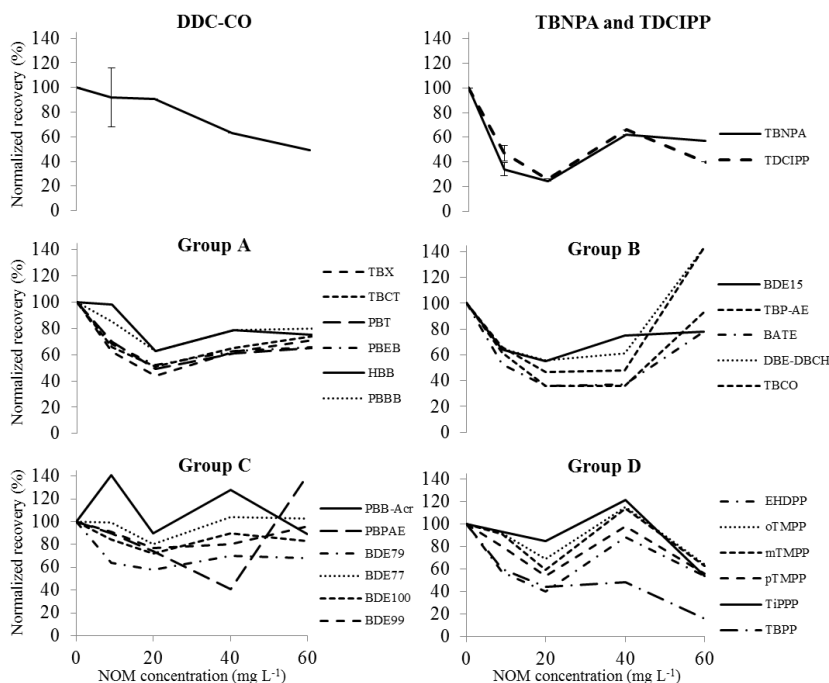


Figure 5 Normalised recovery (%) of flame retardants (FRs) in the natural organic matter (NOM) experiment (concentration 0 mg L⁻¹ = 100% recovery), as a function of NOM concentration for different FRs, which were grouped based on PCA and HCA in Paper II. Triplicate results for 9 mg NOM L⁻¹ are shown for the compounds DDC-CO, TBNPA and TDCIPP, and average recoveries and standard deviations are listed for all compounds in Table S15 in the Supporting Information to Paper II. Source: Paper II.

4.1.2 Clean-up (Paper I)

As shown in the NOM experiment (Paper II), clean-up is an essential part of an analytical method, especially when the matrix is complex, such as in natural waters. When extracts from the NOM experiment were analysed without any clean-up, interferences from the matrix resulted in wide and distorted peaks, making evaluation of the data highly challenging (results not shown). To cope with this, three different clean-up methods (Florisisil[®], acidified silica and alumina) were tested for their suitability in removing the interferences with minimal losses of the analytes. The results showed that all three clean-up methods resulted in relatively clean extracts, as judged from the

chromatographic shape of peaks and background noise. However, the FR recoveries were highly influenced by the choice of clean-up method. For example, all OPFRs, allyl 2,4,6-tribromophenyl ether (TBP-AE), PBPAE and PBB-Acr showed low recoveries (<30%) when using acidified silica, which is likely due to degradation under acidic conditions. Moreover, a few OPFRs (tripropyl phosphate (TPP), tributyl phosphate (TNBP) and TCIPP) showed low recoveries also when using Florisil[®], while TPP also showed low recoveries when employing alumina. Overall, OPFRs showed lower recoveries (mean 40%) than PBDEs (98%) and HFRs (91%) for all three clean-up methods. As discussed in Paper I and elsewhere (Liang *et al.*, 2015), this can possibly be explained by the fact that OPFRs are prone to adsorb to glass surfaces, despite all surfaces in direct contact with the sample being rinsed carefully with organic solvent. Based on the results obtained, alumina was concluded to be the most suitable clean-up material and was therefore used in Papers II, III and IV.

4.1.3 Instrumental analysis (Paper I)

In Paper I, GC coupled to three different MS setups (EI-MS/MS, EI-MS and CI-MS) was tested for the ability to detect a large number of FRs. Of the 102 FRs tested, it proved possible to detect 88, 83 and 78 FRs using EI-MS/MS, EI-MS and CI-MS, respectively (Table S10 in the Supporting Information to Paper I). In total, 10 FRs could not be detected with any of the instrumental techniques, which can be explained by thermal decomposition or too low volatility of the FR to be eluted (Fialkov *et al.*, 2007). Other potential explanations may be poor ionisation in the ion source or insufficient retention on the column. PBDEs showed detectable peaks on all instruments, which was expected since all three instrumental techniques have been used for PBDE analysis in previous studies (Guerra *et al.*, 2010, Covaci *et al.*, 2002, Cristale & Lacorte, 2013, Cristale *et al.*, 2012). The highest number of HFRs was detected with CI-MS (42 out of 46), followed by EI-MS/MS (40/46) and EI-MS (36/46). Thermal degradation was observed for PBPAE when using split/splitless injector (300 °C). To prevent this degradation, the injector was changed to a multimode inlet (MMI) injector, which was used for all further analyses within this thesis. For OPFRs, EI-MS/MS was able to detect the highest number of compounds (21 out of 29), followed by EI-MS (20) and CI-MS (12). One important finding in Paper I was that the bromine ion isotopes (m/z 79 and 81) were the major fragments for 26 out of 42 HFRs and for all PBDEs when analysed with CI-MS. This is an important observation, since these fragments often offer high selectivity, but co-elution with other FRs or

bromine-containing matrix may cause problems, since separation by choosing specific mass fragments cannot be achieved (Thorenz *et al.*, 2010, Marsh *et al.*, 2004). Thus, one of the main advantages of MS is lost on choosing CI-MS for the analysis of HFRs and PBDEs, and hence extra caution is needed to avoid reporting falsely high concentrations due to co-elution of other brominated compounds. Alternatively, more effort is needed to achieve optimal separation on the GC column. Furthermore, the use of fragments other than the bromine isotopes strengthens the identification potential, as structural information is provided (Cristale *et al.*, 2012). In addition, the fact that the bromine isotopes are the major fragments for many HFRs and PBDEs makes the use of isotopically labelled internal standards complicated, since the monitored ions are not specific for the isotopically labelled standard. Finally, no difference in terms of selectivity was found between EI-MS/MS and EI-MS, although it is generally known that tandem MS is more selective than single MS (de Dobbeleer *et al.*, 2012, Harris, 2007).

Instrumental detection limits (IDLs) were used to compare the three instrumental set-ups in terms of detection ability (*i.e.* the ability to detect low concentrations (Fialkov *et al.*, 2007)), defined here as the amount of analyte that is detectable and distinguishable from the background with 95% probability (Wells *et al.*, 2011). In general, EI-MS/MS provided the lowest (*i.e.* the best) IDLs for most PBDEs (5 out of 6) and HFRs (23 out of 26), while EI-MS provided the lowest IDLs for most OPFRs (8 out of 13) (Figure 6). CI-MS generally provided lower IDLs than EI-MS for the HFRs, although there were exceptions (Figure 6). For OPFRs, only small differences in detectability between EI-MS and EI-MS/MS were observed. TDCIPP, TCIPP and TTBNPP were the only OPFRs detected with CI-MS. This can be explained by those OPFRs being halogenated and by the fact that CI-MS has high response factors for compounds containing halogens (de Hoffman & Stroobant, 2007). BDE209 was detected using EI-MS and CI-MS but not using EI-MS/MS, which might be due to the longer flight path (including a collision cell) within the EI-MS/MS, which results in a higher risk of decomposition of this relatively labile FR (Paper I).

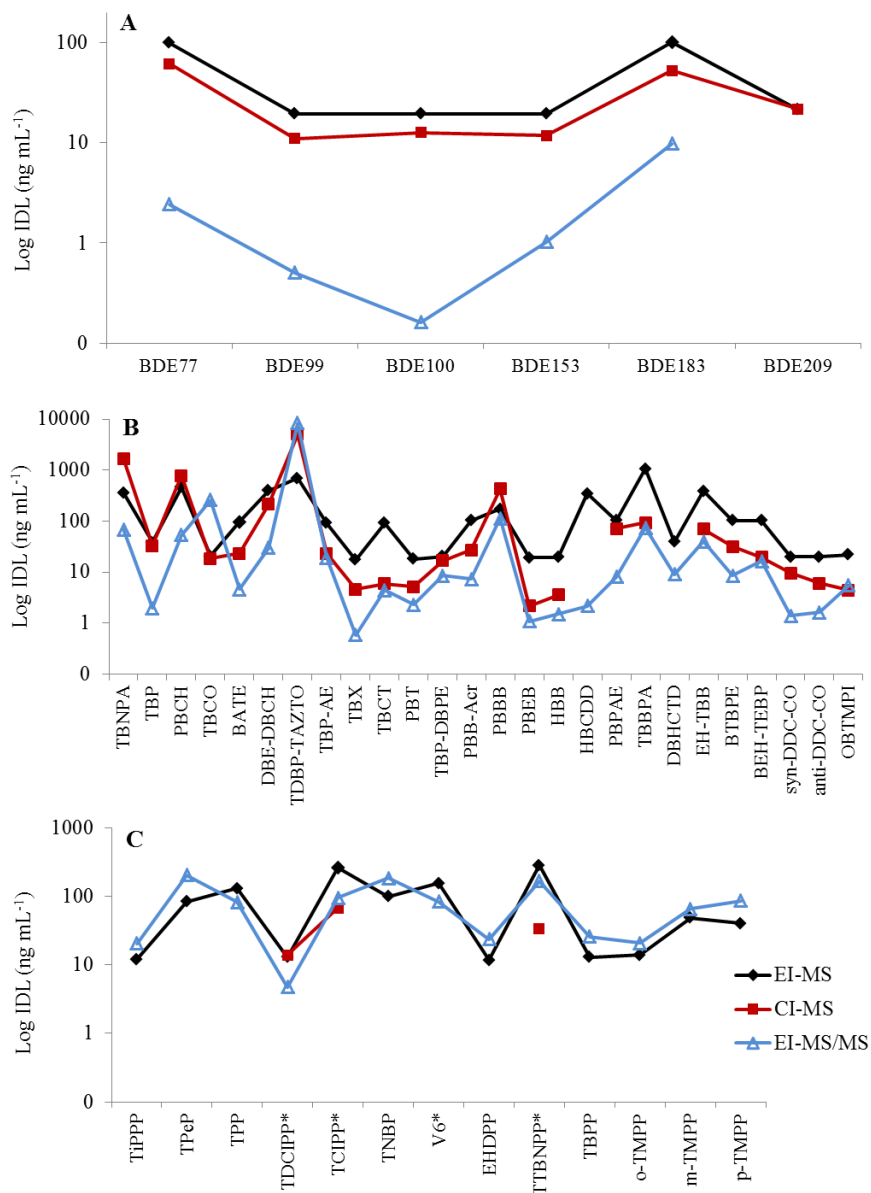


Figure 6. Log-transformed instrumental detection limits (IDLs) for targeted flame retardants (FRs): (A) PBDEs, (B) HFRs and (C) OPFRs, using GC-EI-MS, GC-(CI)MS, and GC-(EI)MS/MS. Missing data point indicates that the FR was not detected at the chosen concentration level; *Halogenated OPFR. Source: Modified version of Figure 2 in Paper I.

The influence of matrix on the instrument signal was investigated using the GC-(ED)MS configuration by comparing the instrumental response of a spiked river extract with a pure solvent standard spiked with the same FR concentrations as the river extract (~10 times LOD). Matrix effects (ME) were observed for most FRs analysed, of which 25 out of 45 showed enhancement ($ME \geq 1.1$) and five out of 45 showed suppression ($ME \leq 0.9$). For the PBDEs, the heavier compounds (*i.e.* BDE153, 183 and 209) showed an enhanced signal with increasing bromination, while the lighter PBDEs (*i.e.* 77, 99 and 100) only showed minor or no ME (Figure S2 in the Supporting Information to Paper I). For HFRs, 18 compounds showed enhancement, three showed suppression and five were unaffected. Regarding the OPFRs, four compounds showed enhancement, two showed suppression and seven showed no ME. As discussed in Paper I, there are several possible causes of matrix enhancement, including the masking of active sites by matrix in the injector, which may result in more complete transfer of the analytes to the column (Erney *et al.*, 1993) and also possible co-elution of the analyte with other hydrocarbons, *e.g.* NOM, which can potentially form the same fragment as the analyte, thus causing an enhanced signal. Furthermore, matrix suppression can be explained by degradation of analyte due to reaction with non-vaporising matrix components accumulated in the injector (Hajšlová *et al.*, 1998). Pearson correlation was used to further analyse the relationship between the physicochemical properties of the FRs and the corresponding ME. For PBDEs, the ME was positively correlated with many properties, *e.g.* retention time and boiling point. Both of these correlations can probably be attributed to the increased column bleeding with increasing GC oven temperature, resulting in higher chemical noise for late eluting, heavier PBDE congeners. Moreover, heavier compounds with a higher boiling point spend a longer time in the liner, leading to more time for them to react with active sites within the liner. For HFRs and OPFRs, no significant correlations were observed, which is likely due to higher structural and functional diversity of those FRs compared with the PBDEs.

Comparing the MEs of the different FR groups obtained from the PCA and HCA in Paper II (Group A-D, TBNPA, TDCIPP and DDC-CO), no clear conclusions could be drawn (Figure 7). Nevertheless, the three FRs (2-ethylhexyl diphenyl phosphate (EHDPP), tris(4-tert-butylphenyl) phosphate (TBPP) and PBB-Acr) showing the largest matrix enhancement are all capable of forming strong hydrogen bonds, which indicates that hydrogen bonds may play an important role, not only in the interaction with NOM, but also for the MEs observed during instrumental analysis. However, other FRs also capable of forming this type of bond did not show any ME. Thus, ME is a complex

phenomenon that cannot be explained by only one mechanism but rather by several co-existing mechanisms, including different type of interactions (such as strong hydrogen bonds) with the liner and matrix components. Moreover, it is likely that MEs vary substantially from matrix to matrix. Hence, for accurate measurements, it is crucial to use adequate compensatory measures. As discussed in Paper I, matrix-matched calibration was evaluated and proved to be an adequate way of compensating for MEs.

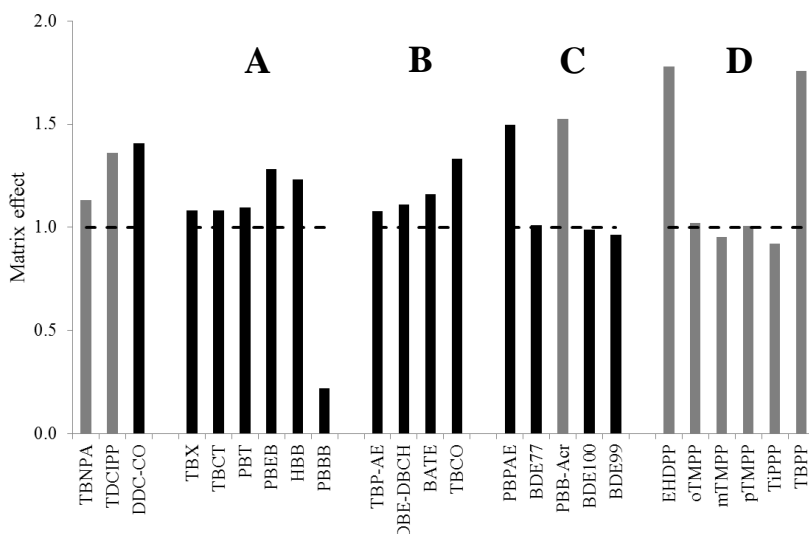


Figure 7. Matrix effects (MEs) of flame retardants (FRs) divided into groups (A-D) based on the PCA/HCA in Paper II, in order of increasing GC retention time per group. Bars representing FRs capable of forming strong hydrogen bonds are shown in grey. The dashed line represents ME=1, *i.e.* no observed matrix effect. Source: Modified version of Figure S2 in the Supporting Information to Paper I.

4.2 Sources and trends of flame retardants (Paper III)

4.2.1 Levels of flame retardants in Swedish rivers

In the screening study of Swedish rivers described in Paper III, FRs were found to be ubiquitously spread, with detectable amounts in all sampled rivers. Of 61 FRs analysed, 26 were detected in at least one river. Generally, both higher variability and higher concentrations were observed in southern rivers

(latitude < 62°N) compared with northern rivers (latitude > 62°N). Pearson correlation analysis was carried out, including the concentrations of the FRs and a number of potential explanatory variables (*i.e.* latitude, catchment area, water temperature, population density, total catchment population, river discharge, surface runoff, dissolved organic carbon (DOC) concentration and suspended particulate matter (SPM) concentration). It was found that the higher population density in southern Sweden best explained the higher levels of FRs in the south. Σ FR concentrations ranged up to 170 ng L⁻¹, with an average concentration in all rivers of 31 ± 45 ng L⁻¹. The total concentrations in Swedish rivers are generally lower than measured concentrations in many other European (Andersson *et al.*, 2013, Martínez-Carballo *et al.*, 2007, Wolschke *et al.*, 2015, Cristale *et al.*, 2012) and Chinese rivers (Wang *et al.*, 2015).

Two OPFRs, TDCIPP and tris(2-ethylhexyl) phosphate (TEHP) (quantified as a sum), were detected in all 23 rivers, at concentrations up to 48 ng L⁻¹. As discussed in Paper III, the measured concentrations are likely to derive mainly from TDCIPP (due to the ~6 orders of magnitude lower octanol-water partition coefficient (K_{ow}) of TDCIPP compared with TEHP), but these two FRs are still reported here as combined concentrations. Since TDCIPP/TEHP were detected in both urban and rural areas, this indicates extensive use, possibly in combination with potential for long-range atmospheric transport (LRAT). In a previous literature review (Gustavsson *et al.*, 2017), annual use data were collected from two databases hosted by the Swedish Chemicals Agency (KemI, 2017) and one database hosted by the European Chemicals Agency (ECHA, 2017) (Table 4). According to these databases, 1 000-10 000 tonnes of TDCIPP are used annually within the EU, while no use is reported for Sweden (2015). These data suggest that the TDCIPP/TEHP detected in Sweden are brought there by LRAT or derive from imported goods.

Tris(2-chloroethyl) phosphate (TCEP, another OPFR) was the second most frequently detected FR (56% of the sampled rivers) and showed concentrations up to 14 ng L⁻¹. Again, this FR was detected over the whole latitudinal range of Sweden, which might indicate LRAT. The use of TCEP in Sweden is reported to be '4' on an indexed scale of 0-7, where 7 represents high use and 0 represents no use, while, contradictory to this, no use has been reported within the EU (ECHA, 2017). One potential explanation for this discrepancy may be differences in the reporting limits of the two databases, as the ECHA database has a higher threshold for when a chemical needs to be registered.

Both TBBPA and PBT were detected in 44% of the rivers studied. This shows that not only OPFRs, but also HFRs, are widely spread in Swedish rivers. TBBPA was almost only detected in the south, at concentrations up to 62 ng L⁻¹. As discussed later (section 4.3), even higher TBBPA concentrations

were detected in streams located in the KCS area (Paper IV). However, these concentrations also included the particulate phase, which was not included in Paper III. According to the chemicals databases, TBBPA has low use in Sweden ('1' on a scale of 0-7), while 1 000-10 000 tonnes are used annually in the EU.

The concentrations of PBT were relatively low, ranging up to 2.5 ng L⁻¹. PBT is not reported to be used in either Sweden or the EU. It may, however, be present in imported goods from other parts of the world and has also been reported as a likely transformation product from other brominated FRs (BFRs), such as DBDPE (Mørskeland, 2010).

Finally, the composition profiles of the FRs showed larger variability in southern rivers than in the north (Figure 3 in Paper III). HFRs were frequently detected in the south but only occasionally in the north. Thus, OPFRs dominated the composition profiles in the northern rivers, which might indicate that OPFRs are more prone to undergo LRAT than HFRs.

Table 4. Annual use of organic flame retardants in Sweden (indexed value for 2015)^{a,b} and the European Union (tonnes)^{b,c}. The Swedish use is indexed (due to confidentiality) on a scale 0-7, where 7 represents high use and 0 no use. For compound abbreviations, see Tables 1-3.

Compound	Sweden (use scale) ^{a,b}	EU (tonnes) ^{b,c}
BTBPE	4	NA
DDC-CO	1	NA
EH-TBB	NA	NA
HBB	NA	NA
PBB-Acr	NA	100-1000
PBT	NA	NA
TBBPA	1	1000-10000
TBP	NA	0
TBX	NA	NA
TCBPA	NA	NA
TEBP-Anh	NA	10-100
<i>m</i> TMPP	NA	NA
<i>o</i> TMPP	3	NA
TCEP	4	0
TCIPP	5	0
TDCIPP	0	1000-10000
TNBP	5	1000-10000
TPHP	5	1000-10000
TTBNPP	3	100-1000

NA=not available; ^aKemI, 2017; ^bGustavsson *et al.*, 2017b, ^cECHA, 2017

4.2.2 Fluxes of flame retardants to the Baltic Sea

The daily flux of FRs from Swedish rivers to the Baltic Sea was estimated to be 8.8 kg day⁻¹, comprising 1.5 kg OPFRs, 7.3 kg HFRs and 0.045 kg PBDEs per day. However, these fluxes should be considered with care, since they are based on one-time grab samples, providing only a snapshot picture. Furthermore, only the apparently dissolved phase was considered. Assuming similar input of FRs from rivers in other countries draining into the Baltic Sea, the total riverine flux of targeted FRs into the Baltic Sea would amount to ~31 kg day⁻¹, comprising ~5.2 kg OPFRs, ~26 kg HFRs and ~0.16 kg PBDEs per day. To the best of my knowledge, river-to-sea fluxes of HFRs have not been reported previously, while some studies for OPFRs exist (Wolschke *et al.*, 2015, Bollmann *et al.*, 2012, Wang *et al.*, 2015). Generally, other studies have reported higher Σ OPFR fluxes than those determined in this study. Fluxes of per- and polyfluoroalkyl substances (Σ PFASs, $n = 13$) from the same rivers have also been estimated and are in the same range (2.8 kg day⁻¹) as the FR fluxes reported here (Nguyen *et al.*, 2017). Among the individual FRs, three HFRs (TBBPA, TEBP-Anh and TBP) showed the highest fluxes to the Baltic Sea, corresponding to 52%, 15% and 9% of the total FR load, respectively.

4.2.3 Point sources of flame retardants

In six rivers, a single FR (TDCIPP/TEHP) was detected. For four of these six rivers, several potential point sources (including WWTPs, landfills and incineration plants) were identified as potential sources upstream of the sampling sites, but for the other two rivers no such potential point sources could be identified. This scarcity of point sources but still frequent detection of TDCIPP/TEHP, in combination with the lack of detection of other FRs, suggests that TDCIPP/TEHP may undergo LRAT. This has also previously been suggested for TDCIPP (Aston *et al.*, 1996). Two rivers showed much higher Σ FR concentrations than the other rivers. For one of the two rivers, the high concentrations can be explained by the sample being collected downstream of a relatively large WWTP. This shows that WWTPs can be important point sources (or source pathways) of FRs. For the other river, a potential explanation for the high value was the close proximity (~2.5 km) to one of the main airports in Sweden. Interestingly, this sampling site showed a similar composition profile to one of the other rivers, where the sample was also collected in the vicinity of an airport. The main FRs detected were TEBP-Anh, tetrachlorobisphenol-A (TCBPA) and TBBPA. To the best of my knowledge, this is the first time TEBP-Anh has been reported as an environmental pollutant. These results indicate that airports may be important

point sources of FRs to the environment. Furthermore, as discussed in Paper III, Pearson correlation was used to investigate correlations between levels of FRs and the number of potential point sources. Several significant correlations were found, but they were mainly driven by individual data points. Nevertheless, this analysis provided an indication that industrial facilities manufacturing chemical products, incineration plants, quarries/mines and animal farms may be point sources of FRs.

4.2.4 Environmental variables

In Paper III, Pearson correlation was also used to investigate correlations among FRs and between FRs and environmental variables (*i.e.* latitude, catchment area, water temperature, population density, total catchment population, river discharge, surface runoff, DOC concentration and SPM concentration). Among the FRs, strong positive correlations were found between the three OPFRs, indicating that these OPFRs are likely to share common sources and are used for similar applications. Significant correlations were also found between OPFRs and one of the HFR (TBBPA), but these correlations were weak. In addition, weak significant correlations were found between OPFRs and PBDEs, while PBDEs were strongly correlated with HFRs. To summarise, these relationships indicate that HFRs and PBDEs share common sources, which may be different from the sources of OPFRs.

Several significant correlations were also found between FR levels and environmental variables. All FRs showed a negative correlation with latitude, although only significant for TCEP, TDCIPP/TEHP and TBBPA, which supports the previous observation of generally higher concentrations in the south than in the north. The same FRs were also significantly correlated with population density. Population density was strongly correlated with latitude and is the likely explanation for the higher FR levels in southern rivers, as higher population density presumably leads to a higher density of FR-containing products. TDCIPP/TEHP (OPFRs) correlated significantly with DOC, which indicates that it may bind to DOC in water. Similarly, it has recently been reported a corresponding relationship for a number of PFASs. However, these PFASs are negatively charged in water and thus likely bind to DOC through ionic bonds. TDCIPP/TEHP are not negatively charged in water and cannot bind to DOC in the same way as PFASs. Instead, based on the observations in Paper II, strong hydrogen bonds are suggested to be a likely mechanism for this interaction. In summary, the significant correlations observed in Paper III indicate that the observed FR contamination in river water occurs as a result of human activities mainly at local/regional scale.

4.3 Flame retardants in a pristine boreal catchment (Paper IV)

4.3.1 Levels in stream and river water

In total, 49 FRs (26 HFRs, 19 OPFRs and 4 PBDEs) were analysed in streams of the KCS area and further downstream. Of those, 10 HFRs, 13 OPFRs and 4 PBDEs were detected in the apparently dissolved phase, while 9 HFRs, 7 OPFRs and 2 PBDEs were detected in the particulate phase. Combined dissolved and particulate concentrations ($\Sigma\text{FR}_{\text{bulk}}$) were highly variable with season and sampling locations (Figure 8). $\Sigma\text{HFR}_{\text{bulk}}$ concentrations (including all sites) ranged up to 320 ng L^{-1} , $\Sigma\text{OPFR}_{\text{bulk}}$ concentrations up to 21 ng L^{-1} and $\Sigma\text{PBDE}_{\text{bulk}}$ concentrations up to 0.073 ng L^{-1} . Mean concentration (\pm standard deviation) was $32 (\pm 65) \text{ ng L}^{-1}$, $3.1 (\pm 4.6) \text{ ng L}^{-1}$ and $0.0014 (\pm 0.0097) \text{ ng L}^{-1}$ of $\Sigma\text{HFR}_{\text{bulk}}$, $\Sigma\text{OPFR}_{\text{bulk}}$ and $\Sigma\text{PBDE}_{\text{bulk}}$, respectively. The PBDE concentrations were in general considerably lower than those of HFRs and OPFRs, possibly reflecting the ban on PBDEs and their replacement with HFRs and OPFRs. However, it could also be a result of the high hydrophobicity of PBDEs, leading to strong terrestrial retention.

The apparently dissolved concentrations ($\Sigma\text{FR}_{\text{dissolved}}$) in the relatively pristine study catchment were generally lower than the concentrations detected in Swedish rivers in Paper III, reflecting fewer point sources compared with the average for Swedish rivers. However, for $\Sigma\text{HFR}_{\text{dissolved}}$ the highest concentrations were found within the pristine catchment, at sites C2 and C4. These comparatively high concentrations (up to 320 ng L^{-1}) at the pristine sites indicate a local point source and may perhaps derive from the research infrastructure used within the catchment. However, further investigation is needed to clarify this. Another possible explanation for the higher concentrations at these first-order stream sites could be the increased input of groundwater with increasing stream order (increasing catchment size), possibly leading to dilution in larger streams, as has been found for total organic carbon (TOC) (Tiwari *et al.*, 2017). Also in Paper III, TBBPA was one of the FRs detected in the highest concentrations, which emphasises the importance of including TBBPA in future environmental monitoring.

The PBDEs were almost exclusively detected in the particulate phase, and thus showed a high partitioning to particles (Tables S11 and S14 in Supporting Information of Paper IV). For HFRs and OPFRs, concentrations were generally higher in the apparently dissolved phase than in the particulate phase. This possibly reflects the overall higher hydrophobicity of PBDEs compared to HFRs and OPFRs.

$\Sigma\text{HFR}_{\text{bulk}}$ concentrations were generally found to be higher at site C16 (the outlet of KCS) than at sites further downstream towards more populated areas (*i.e.* D1, D2 and D3). This could potentially be explained by: i) an increasing contribution of groundwater on moving further downstream (Tiwari *et al.*, 2017), leading to increased dilution at downstream sites, or ii) a higher SPM content at site C16 than at sites D1, D2 and D3. When normalising the $\Sigma\text{HFR}_{\text{particulate}}$ concentrations against SPM instead of water volume, concentrations generally increased further downstream, thus reflecting the increased human impact, although the difference between C16 and D3 was not statistically significant. The $\Sigma\text{OPFR}_{\text{bulk}}$ and $\Sigma\text{PBDE}_{\text{bulk}}$ concentrations remained more or less constant from site C16 and downstream towards D3, both when normalised to water volume and to SPM. This may reflect two counteracting processes, i) increasing dilution with increasing groundwater contribution, and ii) increasing inputs of FRs on moving towards more populated areas.

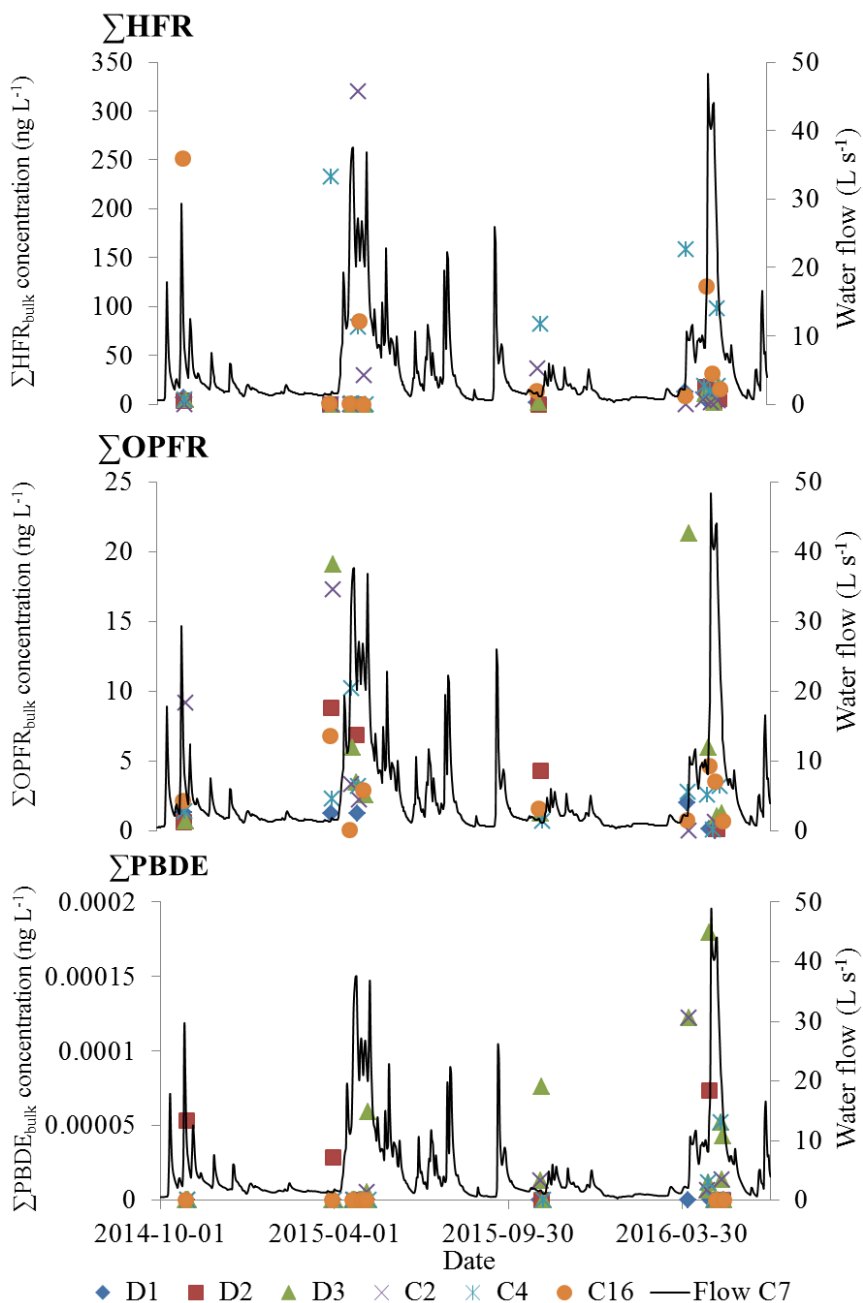


Figure 8. Combined total bulk (particulate + apparently dissolved) concentrations (ng L⁻¹) of organic flame retardants (ΣFRs) at the six sampling sites (C2, C4, C16, D1, D2 and D3) and average daily flow (L s⁻¹) at site C7 (located downstream of the merging point of the streams from C2 and C4). Source: Paper IV.

4.3.2 Impact of hydrological events

Flame retardant concentrations were often elevated during periods of higher flows (Figure 8) compared with periods with lower flows, which is similar to the pattern previously observed for polychlorinated dibenzo-*p*-dioxins/furans (PCDD/Fs), polychlorinated biphenyls (PCBs), hexachlorobenzene (HCB), PAHs and oxy-PAHs in the same catchment (Nguyen *et al.*, *In prep.*, Josefsson *et al.*, 2016). In the present study, FR bulk concentrations were up to 600-fold (mean 62-fold, or 2.3-fold on excluding one extreme value), 3.7-fold (mean 1.1-fold) and 4.9-fold (mean 1.6-fold) higher during spring flood than during snow-covered and snow-free seasons (as average of those two) for Σ HFRs, Σ OPFRs and Σ PBDEs, respectively. On one specific sampling occasion (31 March 2015), Σ OPFR_{bulk} concentrations were elevated at all sites compared with the previous sampling, despite this being almost one week before the actual start of the spring flood. This might be linked to several days of mild weather (average daily temperatures around 0°C) that occurred just before the sampling. This sample likely corresponds to the first meltwater from the snowpack. As elevated concentrations were observed for OPFRs at all sites on this sampling occasion, but only at one site each for HFRs and PBDEs, this indicates that hydrophobicity fractionation (Meyer & Wania, 2008) had occurred within the snowpack, as the OPFRs are generally more water-soluble than HFRs and PBDEs.

4.3.3 Influence of land-cover type

The influence of two land-cover types on retention of FRs was investigated by comparing a completely forested catchment (C2) with a catchment containing a comparatively large proportion (44%) of mires (C4). In general, the mire site showed higher HFR concentrations than the forested site, both for the particulate and the dissolved phase (Figure 3 in Paper IV). In most cases, HFRs were only detected at the mire site. This general trend might be explained by differences in the hydrological flow paths, in combination with vertical differences in the distribution of organic pollutants between the two catchments. More specifically, persistent organic pollutant (POP) concentrations are often highest in the organic-rich top soils of forests and decrease gradually with depth (Bergknut *et al.*, 2010a). In mires, on the other hand, POPs have been shown to have a more even vertical distribution (Bergknut *et al.*, 2010a). During low flow periods, such as during the snow-covered season, stream discharge mainly occurs from lower levels of the forest and mire, and thus POP concentrations can be expected to be higher at the mire site (C4) than at the forested site (C2). Also during spring flood, POP

concentrations can be expected to be higher at the mire site than at the forested site. In the mire, frozen ground thaws slower than in the forest, leading to a larger proportion of overland flow at the mire site. As a result, POPs accumulated in the snowpack on the mire during winter are transported directly to the streams, while POPs from the forested site percolate through the thawed soil to a larger extent and are more likely retained in the ground. These observations are in line with previous observations for PCDD/Fs, PAHs, PAH-derivatives, PCBs and HCB (Josefsson *et al.*, 2016, Nguyen *et al.*, *In prep.*). However, for OPFRs and especially for PBDEs, the forested site (C2) often showed higher concentrations than the mire site (C4) (Figure 3 in Paper IV). For OPFRs, the higher water solubility may lead to a more homogeneous vertical distribution of those compounds also at forested sites (C2), leading to more similar concentrations at sites C2 and C4, and thus more fluctuation in the observed pattern. The PBDEs generally have higher hydrophobicity than the HFRs and it is surprising that they did not show the same trend. The reason for this is unclear and more detailed studies are required. Nevertheless, one possible explanation may lie in the fact that the PBDEs are legacy compounds that are no longer in use. Thus, deposition of PBDEs has probably decreased over the past century, following the declining concentrations observed in urban air (Liu *et al.*, 2016). However, previously deposited compounds still remain in the ground, and over time, this 'plume' of PBDE pollution might have been moving downwards through the soil and is now polluting deeper parts of the soil profile. During the snow-covered season, stream water mainly derives from deeper soil layers (Bergknut *et al.*, 2010b, Laudon *et al.*, 2007), and therefore this may explain the higher concentrations at site C2. At site C4, most of the deposited PBDEs have not penetrated the ground to the same extent, since a larger proportion of the deposited precipitation leaves the mire via overland flow. Moreover, during spring flood, the proportion of snowmelt water at forested sites (such as C2) is smaller (10-30%) than at sites with more mires (>50%) (Laudon *et al.*, 2007). Thus, the stream water at site C2 mainly derives from below ground and may therefore transport the legacy PBDE pollution from the soil into the stream, giving rise to more frequent detection at site C2 than at site C4. However, the vertical distribution of HFRs, OPFRs and PBDEs is currently unknown and, to improve understanding, further investigations are needed.

4.3.4 Potential drivers of flame retardant concentrations in boreal streams and rivers

A number of environmental parameters, including surface runoff, TOC concentration and SPM concentration, were evaluated for their correlation with ΣHFR , ΣOPFR and ΣPBDE concentrations at each of the six field sites (C2, C4, C16, D1, D2 and D3).

Interestingly, positive correlations (although not significant) were found between $\Sigma\text{HFR}_{\text{particulate}}$ concentrations and SPM at sites C16, D1, D2 and D3 (outlet and downstream sites). However, at the headwater sites (C2 and C4; upstream sites), the corresponding correlations were negative. Similar relationships have been observed previously for other organohalogen (hydrophobic) compounds (PCDD/Fs) (Josefsson *et al.*, 2016). As first suggested by Josefsson *et al.* (2016), this might be explained by differences in particle qualities between upstream and downstream sites. Another possible explanation, suggested by Nguyen *et al.* (*in prep.*), is based on chemical equilibrium dynamics. It is possible that the upstream sites have not reached chemical equilibrium or near-equilibrium between FRs and particles, due to the many hydrological processes and the shifting environmental conditions that are at interplay in the headwater catchment (Nguyen *et al.*, *in prep.*). Yet another possible explanation may be the amount of particles. During spring flood, the mean SPM concentration at sites C2 and C4 was 3.0 and 1.0 mg L⁻¹, respectively. At the downstream sites the SPM concentrations were higher, with mean concentration of 130, 8.3, 3.6 and 5.8 mg L⁻¹ for sites C16, D1, D2 and D3, respectively. It is possible that particles have a larger impact on FR concentrations at the downstream sites, while other influencing factors, such as TOC concentration, may be more important at the upstream sites. At the upstream site C4, $\Sigma\text{HFR}_{\text{dissolved}}$ concentrations showed a negative significant correlation with runoff, most likely due to dilution. A negative significant correlation was also observed between runoff and TOC. Although the correlation between $\Sigma\text{HFR}_{\text{dissolved}}$ and TOC was not significant ($p=0.15$, $R=0.49$), it indicates that TOC may be an important factor in controlling apparently dissolved concentrations at the mire site (C4).

5 Conclusions and future research

Analysis of POPs is challenging due to the vast number of compounds that are used in modern society and that are potentially leaking to the environment. One important group of POPs is the FRs, covering a wide range of physicochemical properties, making their analysis particularly challenging. The results presented in this thesis provide a better understanding of how FRs (and especially alternative FRs) are best analysed, including important aspects such as: i) what instrument to choose to reach the lowest possible detection limits, ii) how to perform adequate clean-up of FR-containing extracts, iii) how matrix affects instrumental analysis of FRs, iv) how to extract FRs from water, and v) how NOM influences the extraction of FRs from water. Furthermore, this thesis provides an assessment of the current situation of FR pollution in Sweden, reporting levels of FRs in rivers covering the whole latitudinal range of Sweden and also in streams in a relatively pristine catchment. This will certainly aid future regulatory and remediation efforts. The analytical aspects of this thesis will also aid future environmental monitoring of especially FRs but also of other POPs. Moreover, this thesis has contributed to a better understanding of the environmental behaviour of FRs in the pristine environment by investigating the spatial distribution of FRs in boreal catchments, and the role of spring flood and land-scape type on terrestrial export of FRs to stream and river water. It is my hope that this thesis can become one piece of the puzzle for a less polluted environment.

Of the five sorbents tested (XAD-2, IRA-743, HLB, HR-P and HR-X), HLB eluted with DCM was concluded to be the best choice for the extraction of FRs from water, resulting in the overall highest recoveries. NOM was found to highly influence the recoveries of FRs. For many FRs, both increases and decreases in the recovery were observed with increasing NOM concentrations, suggesting multiple counteracting mechanisms affecting the recovery. Increased recovery with increasing NOM concentration indicates the formation of a NOM-sorbent layer and subsequent interaction of FRs with this layer.

Thus, the formation of a NOM-sorbent layer is suggested to be an important mechanism for the extraction of POPs from NOM-containing waters. Furthermore, the ability to form strong hydrogen bonds appears to be a key mechanism for the interaction between NOM and certain FRs, as exemplified by OPFRs, TBNPA and PBB-Acr. The strong influence of NOM on extraction efficiency stresses the importance of employing adequate compensating measures in order to obtain accurate and reliable results. One such measure is the use of corresponding isotopically labelled standards, but for many 'new' compounds, such as alternative FRs, such labelled standards are often lacking. To circumvent this problem and still be able to compensate for the influence of NOM, the results in this thesis suggest that dividing the compounds into groups based on their properties, followed by the selection of one (or more) isotopically labelled standard for each group, is a relevant approach for compensating for the influence of NOM during extraction.

For many complex matrices, such as NOM-containing water, clean-up is necessary for reducing the influence of matrix during the instrumental analysis. Three different clean-up sorbents (alumina, Florisil[®] and acidified silica) were evaluated in this thesis. Alumina showed the highest overall suitability for FRs with a wide range of physicochemical properties. Florisil[®] also showed high recoveries for PBDEs and HFRs, but was not suitable for OPFRs, while many HFRs and OPFRs showed degradation on acidified silica.

Among the instrumental techniques tested (EI-MS, CI-MS and EI-MS/MS), EI-MS/MS generally provided the lowest detection limits for PBDEs and HFRs, while EI-MS provided the lowest detection limits for OPFRs. Moreover, CI-MS provided lower detection limits than EI-MS for most PBDEs and HFRs. However, for OPFRs, CI-MS proved to be a poor choice, as it failed to detect most OPFRs. Both peak enhancement and suppression were observed due to the presence of matrix. For PBDEs, matrix enhancement correlated significantly with *e.g.* increasing boiling point. A similar relationship was also observed for HFRs and OPFRs, although not significant. Thus, matrix effect reduction is particularly needed when analysing heavier FRs with higher boiling points and longer retention times, and especially if corresponding isotopically labelled internal standards are lacking.

In the screening of FRs in Swedish rivers, both HFRs and OPFRs were frequently detected. HFRs were mainly detected in the south of Sweden, while OPFRs were detected over the whole latitudinal range of Sweden. The detected total FR concentrations ranged up to 170 ng L⁻¹ and in general concentrations were lower than those previously reported for other European rivers. PBDEs were detected in nine rivers, showing that these legacy FRs, despite the ban on use in new products, are still ubiquitously spread in the environment. The

OPFR TDCIPP/(TEHP) was the most frequently detected FR and was detected in all sampled rivers, even where no significant point sources could be identified. This indicates that this FR may undergo LRAT. Two rivers, both located in the proximity of airports, showed detectable concentrations of TEBP-Anh (together with TBBPA and TCBPA), suggesting that airports may be potential point sources of these FRs. To the best of my knowledge, this is the first time that environmental detection of TEBP-Anh has been reported. Correlation analysis showed that HFR and PBDE concentrations correlated strongly with each other, but only weakly with OPFRs. On the other hand, strong correlations were observed among the OPFRs. This suggests that OPFRs may have main sources different from those of HFRs and PBDEs. Finally, population density proved to be a strong predictor of FR levels, explaining the generally higher concentrations observed in southern rivers (latitude<62°N) compared with northern rivers (latitude>62°N). This indicates that human activities at local/regional scale are causing most of the observed FR contamination in river water.

Both within and downstream of the pristine boreal catchment, bulk concentrations (dissolved + particulate) of HFRs, OPFRs, and PBDEs were highly variable with season and sampling location. Bulk concentrations were up to 600-, 3.7-, and 4.9-folds higher for HFRs, OPFRs and PBDEs, respectively, during the spring flood than during low flow seasons (*i.e.* snow-covered and snow-free seasons). Thus, spring flood is an important seasonal event for the fate and transport of FRs in the boreal environment. Moreover, hydrophobicity fractionation was observed during the spring flood in 2015, leading to an early ‘flush-out’ of the more water soluble OPFRs, while PBDEs and HFRs still remained in the snowpack. FR bulk concentrations observed in the present study were generally lower than those reported from larger European rivers, reflecting the relative pristineness of the catchment investigated. However, indications of one (or more) local point sources of TBBPA and TCBPA were observed within the catchment, leading to comparatively high concentrations (up to 320 ng L⁻¹) of those FRs at the two upstream sites (C2 and C4). These two FRs also showed among the highest fluxes to the Baltic Sea in the conducted river screening which indicates the importance of their inclusion in future environmental monitoring. Similar to previous studies of other POPs, there was a general trend that HFR levels were higher at the mire site (C4) than at the forested site (C2), likely attributable to differences in hydrological flow paths and the FR distribution. An increasing FR pollution with increasing human population was indicated by increasing particulate Σ HFR concentrations from the outlet of the pristine catchment (C16) and downwards towards the Baltic Sea when normalized against SPM.

Finally, TOC was indicated to play an important role in the control of apparently dissolved concentrations of Σ HFRs at site C4.

In many cases (and so also in this thesis work), one answered question generates at least three new questions. Thus, there are many possible follow-up studies that may be addressed in future research.

First of all, this thesis deals with the analysis of in total 75 different organic alternative FRs (plus 27 PBDEs). This is a large number of FRs but it is certainly far from all FRs that are used in different flame-amended products. For example, a literature review (Gustavsson *et al.*, 2017) identified 125 alternative FRs, and there are likely to be even more. As a consequence, there is a need for more method development to be able to assess the presence of even more FRs in the environment, which were not included in this thesis. This would preferably also encompass FRs that are better analysed using liquid chromatography (LC), and not only GC compounds. The development of methods would be greatly facilitated if information about FR use in different countries would be available. However, this is rarely the case due to confidentiality, making the environmental analysis of FRs even more challenging as it is currently difficult to know which FRs that should be prioritized when developing analytical methods.

It would be interesting to conduct a similar NOM experiment to the one in Paper II and include also other types of organic pollutants, spanning an even wider range of chemical properties and functional groups, and different types of NOM. This would provide more knowledge about the mechanisms behind the interactions between sorbent and POPs but perhaps even more interesting is to be able to better understand the mechanisms involved in the interactions between POPs and NOM. This is important knowledge as those interactions are affecting the fate and transport of POPs in the environment. As discussed in Paper III, a significant correlation was found between TDCIPP/TEHP and DOC, indicating co-transport of this FR with DOC. The same has previously been observed for a number of PFASs (Nguyen *et al.*, 2017). This is highly interesting and needs to be investigated further – that POPs bind to organic matter is not surprising, but the differences between compounds in their binding warrant more investigations. Moreover, one important mechanism in the environment, that to the best of my knowledge is poorly investigated, is the flocculation of NOM and how it affects the fate and transport of FRs in the environment. This would definitely be interesting to address in future studies and could potentially improve the ability of WWTPs to remove FRs and other POPs from effluent water as flocculation is a common treatment step in many WWTPs.

In the screening of Swedish rivers (Paper III), FRs were detected in all sampled rivers. A number of rivers showed elevated concentrations compared to the other rivers, likely due to point sources located upstream of the sampling sites. Some potential point sources were identified within this thesis and those need to be verified as point sources before any restrictions or remediations can be undertaken. Especially interesting is the detection of TEBP-Anh, TBBPA, and TCBPA in the proximity of two airports. This is, as far as I know, the first time TEBP-Anh has been detected in the environment and the sources of this pollution need to be further investigated. Moreover, following their frequent detection over the whole latitudinal range of Sweden, two OPFRs (TDCIPP/TEHP and TCEP) are suggested in this thesis to be able to undergo LRAT. This needs to be further investigated, *e.g.* by the deployment of atmospheric deposition samplers in remote regions. Also, in Paper IV, the levels of TBBPA and TCBPA were unexpectedly high in the investigated pristine catchment. This demonstrates that we do not know enough about the sources of FRs to the environment and this need to be further investigated.

Furthermore, considering the fatal effects that high levels of POPs can have on top predator populations (exemplified by *e.g.* dichlorodiphenyltrichloroethane (DDT) in eagles (Helander *et al.*, 2008)), top predators are an important group of animals to monitor in order detect compounds with bioaccumulation potential. It would be highly interesting to analyse alternative FRs in *e.g.* blood plasma from eagles or other top predators.

Finally, little is known about the role of microplastics as carriers and contributors of FRs in the aquatic environment and this is something that needs to be investigated.

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Popular science summary

Flame retardants (FRs) are man-made chemicals that are extensively used to prevent fires. During production, FRs are added to many everyday products, such as mobile phones, computers and furniture. The addition of FRs makes the products less flammable, which reduces the risk of fires and thereby the risk of fatalities due to fire. However, FRs can leak from their products and end up in indoor and outdoor environments, where they can cause harm to humans, pets and ecosystems. Many FRs have been found to be environmentally persistent, meaning that they are not easily degraded in the environment but remain for long periods of time. Some FRs are toxic and may undergo bioaccumulation, which leads to accumulation in food webs with the highest concentrations in top predators (such as eagles and bears), posing a threat to their health. Polybrominated diphenyl ethers (PBDEs) is a type of FRs that has been used extensively in the past. Nowadays, the PBDEs are banned from use in new products as a consequence of their harmful properties. Instead, a large number of alternative FRs have been developed in order for product manufacturers to still be able to fulfil the fire-safety legislations. Unfortunately, several of the alternative FRs have been found to be as hazardous for the environment as the forbidden PBDEs. Therefore, there is now an urgent need for new analytical methods to be developed in order to be able to assess which alternative FRs are currently polluting the environment and potentially threatening human and ecosystem health. It is also important to better understand the environmental processes that are affecting the fate and transport of these chemicals and their distribution in the environment. This is largely what this thesis is about.

The first part of this thesis focused on the measurement of FRs using different types of analytical instrumental techniques. Three different instrumental setups representing various measurement techniques were compared for their ability to measure low concentrations of FRs. In chemical trace analysis, the ability to identify the target compounds and accurately

measure low concentration of these is crucial. This challenge can be compared to a bird-watcher looking for birds. If the bird-watcher has a binocular with poor magnification, it will be hard to discover and identify the bird compared to a situation where he/she is using a binocular with a larger magnification. Moreover, other substances present in the analysed sample, such as naturally occurring organic matter, may influence the precision and accuracy of chemical analysis. This challenge could be visualized with a scenario where there are lots of bushes and trees where the bird is sitting. This background, or matrix, will make it more difficult for the bird-watcher to discover the bird than if the bird would sit on an open field with no disturbing matrix. The influence of the so-called matrix effect was investigated in this thesis to clarify how it affects the measurement of FRs. It was found that the effect of the matrix was different for different FRs. For some FRs, the matrix enhanced the signal obtained from the instrument (making it look as if there are more birds than there are), while for other FRs, the signal was reduced (corresponding to a situation where fewer birds are spotted than there actually are). For some FRs, the matrix did not affect the obtained signal, which is the ideal case for the analytical chemist. This is important information for researchers and others measuring FRs, as false assessments of concentrations (or number of birds) highly affect the interpretation of the results. Additionally, three different ways of reducing the matrix were tested to find the most suitable method for clean-up of the environmental samples (water samples) prior to instrumental analysis.

In addition to instrumental analysis, another critical step in the trace analysis of environmental pollutants is the extraction. Extraction is the process of pulling out the target chemical substances from a sample (for example a water sample) into an organic solvent in a substance-specific way, leaving as much as possible of the matrix behind. Apart from matrix reduction, this procedure is necessary for other reasons as well. The target chemical needs to be dissolved in an organic solvent to be able to be measured by the analytical instrument, and by transferring the chemical into an organic solvent, it is possible to concentrate the chemical in a small volume of solvent, which makes the instrumental detection signal stronger and thereby increases accuracy and precision of the measurement. Similarly, it is easier to count ten birds in a small bird cage than if they were spread out in a forest. In this thesis, the extraction was done by pumping the sample (the water) through a sorbent acting as a filter that traps the FRs from the bypassing water. After pumping all the water through the sorbent, the FRs were eluted using an organic solvent, leading to the FRs being removed from the sorbent into the organic solvent. Five different sorbent materials were tested for the extraction of FRs from water in order to find the sorbent with the best trapping ability for FRs.

Furthermore, the influence of matrix in the water sample (more specifically natural organic matter, NOM) on the extraction of FRs from water was investigated. NOM are substances that are formed naturally from for example degrading plants and algae. It is primarily NOM that gives lakes and rivers their brown colour. It was found that the influence of NOM on the extraction was severe, but the impact varied between different FRs, and also depended on the amount of NOM in the water. This is important knowledge because if not properly compensated for, this will lead to false results and interpretations.

In the second half of the thesis, the methods developed in the first part were applied in two field studies. In the first one, the concentrations of FRs in 23 Swedish rivers were measured. The concentrations were generally lower than previously measured levels in other European rivers. Nevertheless, as many as 26 different FRs were found, and there was no river without at least one FR. Generally, a larger number of FRs and higher FR concentrations were found in southern rivers than in northern, reflecting more people living in southern Sweden. Thus, it appears as the FR pollution is highly connected to local sources such as households and waste water treatment plants (WWTPs). However, two FRs was frequently found in rivers from all over Sweden. This suggests that these FRs are transported by air masses from their source regions to more remote locations, such as northern Sweden, where they can be transferred to the ground and into rivers with rain and snow. Interestingly, one specific FR (TEBP-Anh) was found in only two rivers. This is the first time that anyone has found this FR in the environment, and the locations of the sites where it was found suggests that it has been released from nearby airports.

In the second field study, water samples from a relatively remote area in northern Sweden (approximately 60 km northwest of the city Umeå) were collected. This area is less impacted by humans than areas closer to larger cities, and FRs found in this remote area are probably there because of long-range air transport followed by precipitation. The concentrations of FRs were mostly in the lower end of those found in Swedish rivers. Still, although the remote location of the area, as many as 28 FRs were found. Samples were collected during different seasons, and higher concentrations of FRs were observed during the snowmelt period in spring than during the rest of the year. This is an important finding, as knowledge about mobility and transport of organic pollutants will help to predict what will happen with this type of pollution in the future, following for example climate change. Finally, increasing river concentrations when moving downstream towards more densely populated areas were observed for some FRs. This reflects the impact that our human society has on nearby rivers and streams.

Populärvetenskaplig sammanfattning

Flamskyddsmedel är syntetiska kemikalier som används i stor skala för att förebygga bränder. De används som tillsatser i många produkter, som t ex mobiltelefoner, datorer och möbler. De tillsatta flamskyddsmedlen gör att produkterna blir mindre lättantändliga, vilket minskar risken för brand och därmed också risken för dödsfall i samband med brand. Tyvärr läcker de flamskyddande ämnena ofta ut från sina produkter och hamnar i miljön där de kan orsaka skada. Många flamskyddsmedel är svårnedbrytbara och giftiga för organismer. Flamskyddsmedel kan också bioackumulera med höga halter i toppkonsumenter (så som örnar och björnar) som följd, vilket kan leda till försämrad hälsa. Polybromerade difenyletrar (PBDEer) är en typ av flamskyddsmedel som tidigare använts flitigt. Numera har PBDEer förbjudits i nya produkter på grund av deras skadlighet. Istället har ett stort antal alternativa flamskyddsmedel utvecklats för att tillverkare fortfarande ska kunna uppfylla de brandsäkerhetskrav som gäller. Dessvärre har flera alternativa flamskyddsmedel konstaterats vara lika skadliga för miljön som de förbjudna PBDEerna. Därför finns det nu ett stort behov av att utveckla nya analysmetoder för att kunna ta reda på vilka alternativa flamskyddsmedel som förorenar miljön och därmed potentiellt utgör nya hot mot djurs och människors hälsa. Det är också viktigt att skapa grundläggande förståelse av de processer som påverkar spridningen av flamskyddsmedel i miljön. Det är dessa metoder och denna förståelse som den här avhandlingen handlar om.

Den första delen av denna avhandling ägnades åt metodutveckling för haltbestämning av flamskyddsmedel i vatten, dvs mätning av mängden flamskyddsmedel per volymenhet (per liter). Tre olika instrumentella system jämfördes med avseende på deras förmåga att mäta låga koncentrationer av flamskyddsmedel. När man genomför analys av föroreningar i miljöprover är denna förmåga central. Detta kan liknas vid en fågelskådare som letar efter fåglar. Om fågelskådaren har en kikare som enbart ger en liten förstoring så kommer det vara betydligt svårare att hitta fåglarna än om fågelskådaren har en

kikare med kraftigare förstoring. Vidare så kan andra ämnen som finns i miljöprover (t ex naturligt förekommande organiskt material) påverka den kemiska analysen. Detta kan liknas vid att det är många buskar och träd där fåglarna uppehåller sig. Denna bakgrund, eller matris, gör det svårare för fågelskådaren att se och identifiera fåglarna än om de skulle sitta på ett öppet fält. Denna så kallade matriseffekt undersöktes för att bättre förstå hur bakgrundsämnen påverkar analysen av flamskyddsmedel vid instrumentell analys. För vissa flamskyddsmedel gjorde matrisen att signalen i instrumentet ökade (så att det såg ut som det var fler fåglar än vad det egentligen var i verkligheten), medan för andra flamskyddsmedel minskade istället signalen (så att en del fåglar missades). För ytterligare andra flamskyddsmedel påverkades inte analysen av matrisen alls. Detta är viktig ny kunskap för forskare och andra som mäter halter av flamskyddsmedel i miljön eftersom felaktiga resultat kan leda till felaktiga tolkningar och beslut.

Ett annat viktigt steg vid analys av föroreningar i miljöprover är extraktion. Målet med extraktionen är att förflytta de kemiska ämnen man vill analysera till ett organiskt lösningsmedel, t ex från att ha varit löst i vatten till att bli löst i metanol, samtidigt som man försöker bli av med så mycket av miljömatriken som möjligt. Detta är nödvändigt av flera anledningar. Först och främst måste de ämnen som ska analyseras vara lösta i ett organiskt lösningsmedel för att kunna mätas med analysinstrumentet. Extraktionen möjliggör också att ämnena som ska analyseras kan koncentreras till en högre halt vilket underlättar den instrumentella analysen. Detta kan liknas vid att det är lättare att räkna tio fåglar i en liten bur än i en hel skog. I den här avhandlingen utfördes extraktionen genom att pumpa vattenprovet genom en sorbent (ett slags filter) som fångade upp flamskyddsmedlen medan vattnet passerade igenom. Efter att allt vatten hade pumpats igenom så sköljdes flamskyddsmedlen ut med hjälp av ett organiskt lösningsmedel. Fem olika sorbent-material testades för att finna det bästa alternativet för analys av vatten som förorenats med en mängd olika flamskyddsmedel. Vidare undersöktes hur matrisen (mer specifikt naturligt organiskt material, NOM) påverkar själva extraktionen av olika flamskyddsmedel. NOM är substanser som bildas naturligt från exempelvis växter och alger. Det är i huvudsak NOM som ger många sjöar dess bruna färg. I studien konstaterades det att NOM påverkar extraktionen i hög grad, men exakt hur mycket beror på vilket flamskyddsmedel det handlar om och hur mycket NOM som finns i vattenprovet. Detta är viktig kunskap eftersom om man inte kompenserar på rätt sätt för den påverkan som NOM har på extraktionen, så leder det till felaktiga resultat och tolkningar.

I andra delen av avhandlingen så tillämpades de metoder som testats fram i första delen genom två fältstudier. I ett arbete provtogs 23 svenska åar/älvar för

att undersöka förekomsten av flamskyddsmedel. Koncentrationerna var generellt sett lägre än vad som tidigare hittats i andra europeiska vattendrag. Trots detta hittades så många som 26 olika flamskyddsmedel, och i varje vattendrag detekterades minst ett flamskyddsmedel. Generellt så hittades fler flamskyddsmedel i åar från södra Sverige, och koncentrationerna där var också högre än i nordligt belägna åar/älvar. Detta kan förklaras med att fler människor bor i södra Sverige. Det verkar alltså som att förorening av flamskyddsmedel är starkt knuten till utsläppskällor som hushåll och avloppsreningsverk. Ett av flamskyddsmedlen detekterades i alla åar/älvar, vilket tyder på att detta ämne kan transporteras via lufttransport till avlägsna platser, som t ex norra Sverige, och sedan följa med regn och snö ner till mark och vattendrag. En intressant observation var att ett av de studerade flamskyddsmedlen (TEBP-Anh) enbart hittades i två älvar. Detta är de första fynden av just det här flamskyddsmedlet i miljön, och fyndplatserna tyder på att den här föroreningen skulle kunna komma från två närliggande flygplatser. I den andra fältstudien togs vattenprover från ett relativt avlägset avrinningsområde i norra Sverige (ca 60 km nordväst om Umeå). Detta område är relativt sett mindre påverkat av mänsklig aktivitet än områden närmare större städer. Flamskyddsmedel som hittas där har förmodligen transporterats dit med luften och fallit ned tillsammans med partiklar och nederbörd. I detta område var koncentrationerna generellt sett lägre än de koncentrationer vi fann i de svenska åarna/älvarna, vilket kan förklaras med mindre mänsklig påverkan. Koncentrationerna av flamskyddsmedel var ofta högre under snösmältningen på våren jämfört med under resterande delar av året. Kunskap kring säsongsvariationer av föroreningshalter i vatten är viktig att ha i många sammanhang, t ex då transport av miljöföroreningar ska beräknas och förutspås med och utan klimatförändringar. Vidare konstaterades att koncentrationerna av vissa flamskyddsmedel ökade nedströms mot mer befolkade områden. Detta visar att vårt mänskliga samhälle har stor påverkan på vattenkvaliteten i älvar och åar.

Acknowledgements

Now the time has come for me to summarize my PhD (I know, it's weird, huh?). The major highlights during those almost 5 years as a PhD student include (in addition to all the FIKAs of course) conference trips to Dioxin in Sao Paolo and Vancouver and a trip to Vietnam (not work-related though, despite nice company from Minh, Lutz, Sarah and José). Vietnamese night trains are great, right Minh? Of course, also my first and second accepted papers (as main author) are important highlights of my PhD studies. I have also experienced some down-periods during this time but thanks to all the awesome people around me, I have made my way back up again☺ In the following section I would like to thank all those amazing people that have made my PhD time to such a wonderful period of my life. I could not have done it without you!

To start with, I would like to thank my four supervisors for their excellent supervision. I have really enjoyed working with you (and it is not over yet!) and I have especially enjoyed all the meetings we had when planning experiments and discussing results. It has been so much fun and so inspiring working with you! **Karin Wiberg**, not my biological mother but for sure my scientific mother. Thanks a lot for caring so much about us, your students, and for always making sure that my PhD project was going in the right direction. Thank you also for reading my manuscripts so thoroughly and for your great support and genuine interest in research! **Lutz Ahrens**, thank you so much for always being available to answer all kinds of questions that popped into my head and for always having a solution to every single problem. Even though you were always extremely busy, you always made time for me (and the other students) and you have never ever made me feel that I was disturbing you (even though I probably did). I really appreciate all your help! **Sarah Josefsen**, thank you for all your bright ideas and suggestions, and for being such an inspiring person. It is a shame that we don't have you at work anymore but I am really happy that you still wanted to continue supervising me and

Minh. **Dan Berggren Kleja**, thank you for always being ready to answer my NOM-related questions. It has been great to have you on board and I have been feeling safe with all your great knowledge about soils and NOM. Thank you!

In addition to my supervisors, there have been a large bunch of awesome people supporting me during my PhD studies. First of all and certainly not least, **Minh Anh Nguyen**, my brother from another mother, father and continent! It has been so much fun working with you, having FIKA with you, and running around in the lab with you! I will certainly remember all the nice FIKAs, (cookie) sampling campaigns, and all our discussions about science and non-science. Thank you so much for your support and for making it so much fun going to work every single day! Thanks to **Wiebke** (there is never a boring lunch/fika when you are around), **Rikard** (if you only take half as good care of Edvard as you do of the QTOF, Edvard is the luckiest kid in the world), **Vera** (long live Brännboll!), **Mattias** (I know where you are hiding all the cups...), and **Frank** (good luck with the landhockey, I should try it sometime), all important parts of the POPs-family! Big thanks also to the rest of the POPs-family, including **Anna-Karin** (GC is more fun than LC, right?), **Pablo** (aka Dr. Non-target), **Jana** (jag vill också klappa katter på jobbet!), **Lisa** (thanks for always being so friendly and for taking so good care of the lab and extracting so many samples for me!), **Laura** (I am convinced that you will finish the Swedish classic, you are strong!), **Oksana** (I still haven't understood where you are from but it is anyway nice that you are here!), **Meri** (nicest laughter in the world!) and **Anastasia** (I think you are the only person I have met from Moldova and based on this one replicate, Moldavian people seem to be nice!). Speaking about awesome people, I should not forget all the other previous and current PhD students at the department: **Alexander** (do you need to buy lunch today?), **Didier** (when you have moved back to Uppsala, we can go for burgers more often!), **José** (just a small town girl, livin' in a lonely world... you do this one so good!), **Salar** (vad var det jag sa? CrossFit är kul!), **Elin** (I haven't seen you in a long time, I guess you are high up in the sky somewhere?), **Amélie** (sage de me choisir pour arroser vos plants de tomate!), **Kristina** (tack vare dig vet jag vad vattenpest är), **Hannah** (how is Norway? I am looking forward to hear you speak Norwegian when you are back), **Sophia** (aka the dancing queen), **Bonnie** (my Bonnie is over the ocean, my Bonnie is over the Sea... do you know this song?), **Maidul** (Sir, you are such a nice guy!), **Jenny** (so nice that you have fully embraced our FIKA tradition), **James** (is the weather better here than in UK?), **Claudia** (it is amazing how fast you can talk and formulate sentences), **Emma L** (I am still impressed of your determination in training for the marathon), **Pianpian** (congratulations to your PhD!), **Oskar** (have you shot any moose lately?), **Oded** (how is it going with your facial recognition dating

site?), **Steffi** (it is hard to find anyone nicer than you, coming back soon?), **Ana V** (I don't know to whom I should complain about the wind in the face now when you are not around) and **Sara** (kul att du blivit en i gänget!). Big thanks to all of you for all the support and laughter!

Thanks to **Alina** for i) extracting so many of my samples, ii) asking me out, and iii) being such a wonderful and amazing person! Thanks to **Joachim** (have you got webbing between your fingers yet?), **Jelena** (you will be a great PhD student, even though you joined the dark, muddy side...), **Sara Goncalves** (welcome back! And thanks for your amazing cooking/baking skills), **Nadine** and **Miriam** (where are the two of you? We miss you!), **Svenja** (thanks for always spreading so much positive energy), **Francoise** (it starts with brännboll and continues with heavier stuff... be careful), Dr. **Frank** (I am still waiting for your haka...), **Emil** (probably the best GIS-guy in the world), **Gustav** (du säger väl till när Folkvang spelar i Uppsala?), **Simon** (it was great running with you, we should do it again sometime), **Anna-Leena** (kul att träffa dig igen!), **Ande** (I like your new hair color) and all the other amazing people that have shared so many FIKAs and lunches with me and that very often made them the highlights of my day.

Thanks to **Erik Ribeli** for the master thesis work that resulted not only in one but two publications (soon)! Thank you also for the beautiful drawing covering the front of this thesis. Thanks to Greta and Nicholas for help with sampling and laboratory work, and also big thanks to the personnel at Svartberget field station for help with sampling. Believe it or not, but sometimes chemical instruments does not behave as you want them to, luckily I got great support from **Henrik**, **Emma**, **Märit**, **Ove**, and **Elin**, thanks a lot! Thanks to **Willem** and **Jenny** for running the department and section in such a fabulous way, and finally, big thanks, high-fives and chest-bumps to **CrossFit Uppsala** for by making me physically stronger also have made me mentally stronger, and for providing me with such a fun and efficient way of stress release.

Till sist så skulle jag vilja avsluta med att tacka min kära familj (**Mamma**, **Pappa**, **Sandra** och **Marcus**) för allt det stöd ni har gett mig genom åren. Det har verkligen varit guld värt! Tack också till **farmor** för alla trevliga fikastunder du bjudit på under hela min uppväxt ☺

Disclaimer: In case I forgot someone, I am very grateful to that person too!